PB-242 861

WATER POLLUTION INVESTIGATION: ASHTABULA AREA

P. Michael Terlecky, Jr., et al

Calspan Corporation

Prepared for:

Environmental Protection Agency

January 1975

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EPA-905/9-74-008

WATER POLLUTION INVESTIGATION: ASHTABULA AREA

CALSPAN INC.

U.S. ENVIRONMENTAL PROTECTION AGENCY
REGION V ENFORCEMENT DIVISION
GREAT LAKES INITIATIVE CONTRACT PROGRAM

JANUARY 1975

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BIBLIOGRAPHIC DATA SHEET

1. Report No. EPA-905/9-74-008

2.

3. Recipient's Accession No. PB242861

4. Title and Subtitle

Water Pollution Investigation: Ashtabula Area

5. Report Date January 1975

6.

7. Author(s)

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8. Performing Organization Rept. No. ND-5358-M2

9. Performing Organization Name and Address

Calspan Corporation
Buffalo, New York 14221

10. Project/Task/Work Unit No.

11. Contract/Grant No. EPA-68-01-1575

12. Sponsoring Organization Name and Address

U.S. Environmental Protection Agency, Region V
Enforcement Division

13. Type of Report & Period Covered Final

14.

15. Supplementary Notes

EPA Project Officer: Howard Zar

16. Abstracts

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The quality of water passing through the Ashtabula complex including Fields Brook has been recognized for many years as a serious environmental problem. NPDES permits have been issued during 1973 and 1974 for an industrial complex of nine major industries. Total residual chlorine, mercury, dissolved solids, and metals content appear to be the most serious water quality parameters which affect this area. Measurement of these parameters from the harbor to Fields Brook demonstrate the source of the materials. Commonly observed values of mercury in Fields Brook

(continued next page)

17. Key Words and Document Analysis. 17a. Descriptors

Water Quality, Aquatic Biology, Water Pollution

17b. Identifiers/Open-Ended Terms

Fields Brook, Ashtabula River, Lake Erie, Chemical Parameters, Biological Parameters

PRICES SUBJECT TO CHANGE

17c. COSATI Field/Group

18.

1

19. Security Class (This Report) UNCLASSIFIED

20. Security Class (This Page) UNCLASSIFIED

21. No. of Pages 161

22. Price 6.25/2.25

ABSTRACT (continued)

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If the requirements of current NPDES permits are met for the 1976-1977 period, improvements can be expected in the water quality of the area. Further improvement in the reduction of pollutants in the 1977-1983 period is also expected.

Continued monitoring of the total residual chlorine, mercury, conductivity and dissolved solids during the next two years is recommended.

WATER POLLUTION INVESTIGATION: ASHTABULA AREA

by

P. Michael Terlecky, Jr.
John G. Michalovic
Sharon L. Pek

CALSPAN CORPORATION

In fulfillment of

EPA Contract No. 68-01-1575

for the

ENVIRONMENTAL PROTECTION AGENCY

Region V

Great Lakes Initiative Contract Program

Report Number: EPA-905/9-74-008

EPA Project Officer: Howard Zar

January 1975

This report has been developed under auspices of the Great Lakes Initiative Contract Program. The purpose of the Program is to obtain additional data regarding the present nature and trends in water quality, aquatic life, and waste loadings in areas of the Great Lakes with the worst water pollution problems. The data thus obtained is being used to assist in the development of waste discharge permits under provisions of the Federal Water Pollution Control Act Amendments of 1972 and in meeting commitments under the Great Lakes Water Quality Agreement between the U.S. and Canada for accelerated effort to abate and control water pollution in the Great Lakes.

This report has been reviewed by the Enforcement Division, Region V, Environmental Protection Agency and approved for publication. Approval does not signify that the contents necessarily reflect the views of the Environmental Protection Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

ABSTRACT

This investigation reports the results of a historical data collection of information concerning the lower Ashtabula River, Harbor and nearshore area, a detailed water sampling and biota collection made during 1973 and 1974, and an evaluation of present and future discharges on the water quality and biota of the area.

The quality of water passing through the Ashtabula complex including Fields Brook has been recognized for many years as a serious environmental problem. NPDES permits have been issued during 1973 and 1974 for an industrial complex of nine major industries. Total residual chlorine, mercury, dissolved solids, and metals content appear to be the most serious water quality parameters which affect this area. Measurement of these parameters from the harbor to Fields Brook demonstrate the source of the materials. Commonly observed values of mercury in Fields Brook were 1.3-1.4 μg/1, although measurements as high as 4.3-4.8 μg/1 were observed. Total residual chlorine values measured at the Fields Brook mouth ranged from 1-12 mg/1 indicating much higher values closer to the source of the discharge. Dissolved solids and conductivity values increased from both the upstream and downstream direction toward Fields Brook. Values of dissolved solids in Fields Brook ranged from 1495 to 1612 mg/1 with corresponding conductivity values ranging as high as 1850 μmho/cm. Flushing time calculations for Ashtabula Harbor during low flow conditions indicated near stagnation for late summer. Diatoms and phytoplankton recovered in the harbor and lower river indicated the presence of a eutrophic, pollution tolerant type of community. Cell counts were found to be low, an observation verified by other researchers. Low biomass, low diversity, and dominance of only a few species at each sample station indicated a seriously degraded water quality situation.

If the requirements of current NPDES permits are met for the 1976-1977 period, improvements can be expected in the water quality of the area.

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ACKNOWLEDGEMENTS

The authors wish to thank Mr. Howard Zar, Project Officer, of the USEPA for his guidance and assistance during the course of this investigation. His many suggestions and comments were useful in the definition of the problem areas and methods of obtaining the data. Mr. Gary Amendola (USEPA-Cleveland) was particularly helpful as to the field aspects of this study and assistance in obtaining previous data. Thanks are due also to Mr. Stasys Rastonis, USEPA, for suggestions made in the early phases of this work. We wish also to thank Mr. Jack Fisher of Calspan for his technical and analytical assistance during the chemical analysis portion of this work. We wish also to acknowledge the cooperation of Mr. Edward Bento, City Manager of Ashtabula, and Mr. Allan Buchler, City Sanitarian. Mr. Donald Sutherland was most cooperative in assistance with logistic arrangements.

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Section 1
INTRODUCTION

This investigation is a detailed examination of one of eleven "special interest" areas designated by the USEPA as worthy of particular attention in the Great Lakes area. The study reported herein basically consists of three parts: first, a presentation in historical perspective the information currently available concerning the water quality and biota of the Ashtabula River, Harbor and nearshore area including the mouth of Fields Brook; second, a report of the results of field investigations conducted by Calspan Corporation during 1973 and 1974; and third, a comparison of these conditions to those expected to exist with the implementation of EPA's NPDES permit requirements and a projection based on current data on whether any actual improvement or changes will occur.

Two reports serve as precursors to this report and form integral parts of this final product: The draft Task I report submitted in final form on 29 October 1973 which serves together with some later additions as Section II of this report; and a report entitled "The Prediction of Free Residual Chlorine Concentrations in a Flowing Stream" (Pereira, Terlecky and Yaksich, 1974) submitted on 30 January 1974 which is included as an Appendix to this report.

The Ashtabula River, located in northeast Ohio, drains generally northward and empties into Ashtabula Harbor on the south shore of Lake Erie. The harbor is located approximately 59 miles east of Cleveland, Ohio and 44 miles west of Erie, Pennsylvania. The general locality is shown on United States Lake Survey Chart Numbers 3, 34, and 342.

The quality of water passing through the Ashtabula complex including Fields Brook has been recognized for many years as a serious environmental problem. Inadequately treated and sometimes raw industrial discharges have seriously degraded the river water quality and illustrate the need for improved treatment methods in the area and the imposition and enforcement of strict standards for effluent and water quality. Fields Brook, a tributary of the lower Ashtabula River exhibits strong medicinal and chemical odors and, at times, white and brown discoloration (Lake Erie Report, 1968).

An industrial complex of nine major industries in the Ashtabula area which discharge to Fields Brook includes the following:

Reactive Metals, Inc. - Sodium and Chlorine Plant
Reactive Metals, Inc. - Metals Reduction Plant
Reactive Metals, Inc. - Extrusion Plant
New Jersey Zinc Co. (formerly Cabot Titania)
Detrex Chemicals - Muriatic Acid Plant
General Tire Co.
Olin Corporation - Chemicals Group
Diamond Shamrock Chemical Co.
Sherwin Williams Chemical Division

The purpose of this report, therefore, is to survey both historical and current data and to determine what measures, if any, might be necessary to improve the water quality and enhance the environmental conditions present for the indigenous biota.

Section 2
SUMMARY

This study has examined the water quality and biota of the lower Ashtabula River and Harbor area both from a historic and current standpoint. The development of an industrial complex discharging into Fields Brook since 1950 has seriously degraded water quality conditions in the study area. Large scale changes in the biota in Fields Brook to a point where the brook is extremely toxic have resulted. This study focused on the water chemistry aspects of the area and included biota sampling to assess the effects of the seriously degraded water conditions in the vicinity of the Fields Brook entrance to the Ashtabula Harbor.

Total residual chlorine, mercury, high temperatures, dissolved solids, and metals content appear to be the most serious water quality parameters which affect this area. Measurements of total residual chlorine in Fields Brook varied from approximately 1 mg/l to 12 mg/l near its mouth. On one occasion a measurement of 35 mg/l total residual chlorine was recorded at an outfall along Fields Brook. Mercury levels in Fields Brook were measured and nearly always exceeded the State of Ohio standard of 0.5 μg/l. In fact, a value of 21 μg/l was recorded. Commonly observed levels of mercury in Fields Brook during this study were 1.3-1.4 μg/l in September 1973. During May 1974 values from 1.4 to 5.8 μg/l Hg were measured near E. 15th St. This occasionally resulted in values as high as 4.3-4.8 μg/l being observed upstream and at offshore stations.

Dissolved solids levels were measured in Fields Brook ranging from 1495 to 1612 mg/l with corresponding conductivity values ranging as high as ≈1850 μmho/cm. A conductivity profile showed the extent of Fields Brook influence of this parameter from the Coast Guard Station to the Penn Central Bridge - a distance of approximately two miles.

Flushing time calculations for Ashtabula Harbor during low flow conditions of the river at 1.5 cfs indicated near stagnation for late summer. A sixty day flushing time was postulated for the harbor under the conditions present at the time.

The absence of an indigenous population suggested the presence of toxicity conditions in the study area. Diatoms and phytoplankton recovered in the harbor and lower river indicated the presence of a eutrophic,pollution tolerant type of community. Cell counts for the entire area appeared to be low, which indicates either dilution (by high lake level) or toxic conditions present. Low biomass, low diversity and dominance of only a few species at each sample station indicated a seriously degraded water quality situation and further supports the conclusion that toxic materials present are affecting the biota.

Section 3

CONCLUSIONS

The most serious water quality problems associated with Fields Brook and the lower Ashtabula River and Harbor are total residual chlorine, mercury and other metals, dissolved solids, and chloride concentrations. Elevated temperatures associated with Fields Brook further degrade the water quality situation. Low cell counts and low biomass throughout the study area support the conclusions based on water chemistry that the levels of pollutants present are toxic to indigenous species.

The effect of Fields Brook on the Ashtabula River and Harbor area decreases with increased distance. Low nutrient loading with the exception of nitrates from Fields Brook and the presence of small amounts of organic material attest to the absence of significant amounts of sanitary wastes although fecal coliform values are occasionally elevated.

Organic chemicals and pesticides were not detected in Fields Brook or the river, although an unknown organic component was traced from Fields Brook to Ashtabula Harbor.

Mercury and total residual chlorine measurements made in May 1974 indicate levels which are in excess of Ohio standards and contribute to conditions which are detrimental to the indigenous aquatic population. If the effluent levels called for by April 1975 are met by local industries, a significant improvement in water quality can be expected in the near term. Temperature effects have not been considered in permits granted to date, and this situation should be reexamined in light of cooling water discharges to Fields Brook and Ohio State stream standards. The final permit for the last remaining industry (which had not received a new permit in 1973) was expected to be issued on December 31, 1974. Lowered levels with respect to chlorine residuals might be expected to be delayed 1-2 years but should be at reduced levels by June 1, 1976. By July 1, 1977, chlorine residual levels should be at levels which will protect aquatic biota, if the requirements of the NPDES permits are met by industries on Fields Brook.

Section 4
RECOMMENDATIONS

Based upon the information gathered in this study, the following recommendations are made with respect to the Fields Brook-Ashtabula River area:

1. A detailed sampling program should be undertaken to define the levels of chlorine present in effluents, Fields Brook, Ashtabula River and Harbor. This study should employ an amperometric titrator to determine free as well as combined residual chlorine. We recommend that the study should begin in July 1975. Results of a 1973 hearing on the conditions in Fields Brook indicate a considerable amount of public interest in solution of the problems associated with effluent discharges. Compliance with issued permits should improve water quality in the area. An area-wide assessment is recommended by State and Federal agencies to evaluate the environmental condition in the Ashtabula River Basin. Results of this assessment could be distributed to the public and include the schedules, construction milestones, and remaining abatement actions which are scheduled by local industries. It is proposed that this assessment be conducted during late 1975.

2. A detailed, comprehensive study preferably with an on-site analysis capability is recommended to be conducted for mercury to determine the source(s) levels and degree of compliance with water quality standards in Fields Brook and the Ashtabula River. This program could be carried on in conjunction with (1) above.

3. The theoretical model developed in Appendix 3 should be field tested and verified to provide a method for predicting chlorine residuals in a flowing stream.

4. Based upon data presented here, the State and Federal Agencies should rigorously enforce effluent levels required in existing permits. Because of the presence of potentially hazardous materials such as mercury and chlorine, continued surveillance is recommended.

Section 5
HISTORICAL DATA ANALYSIS

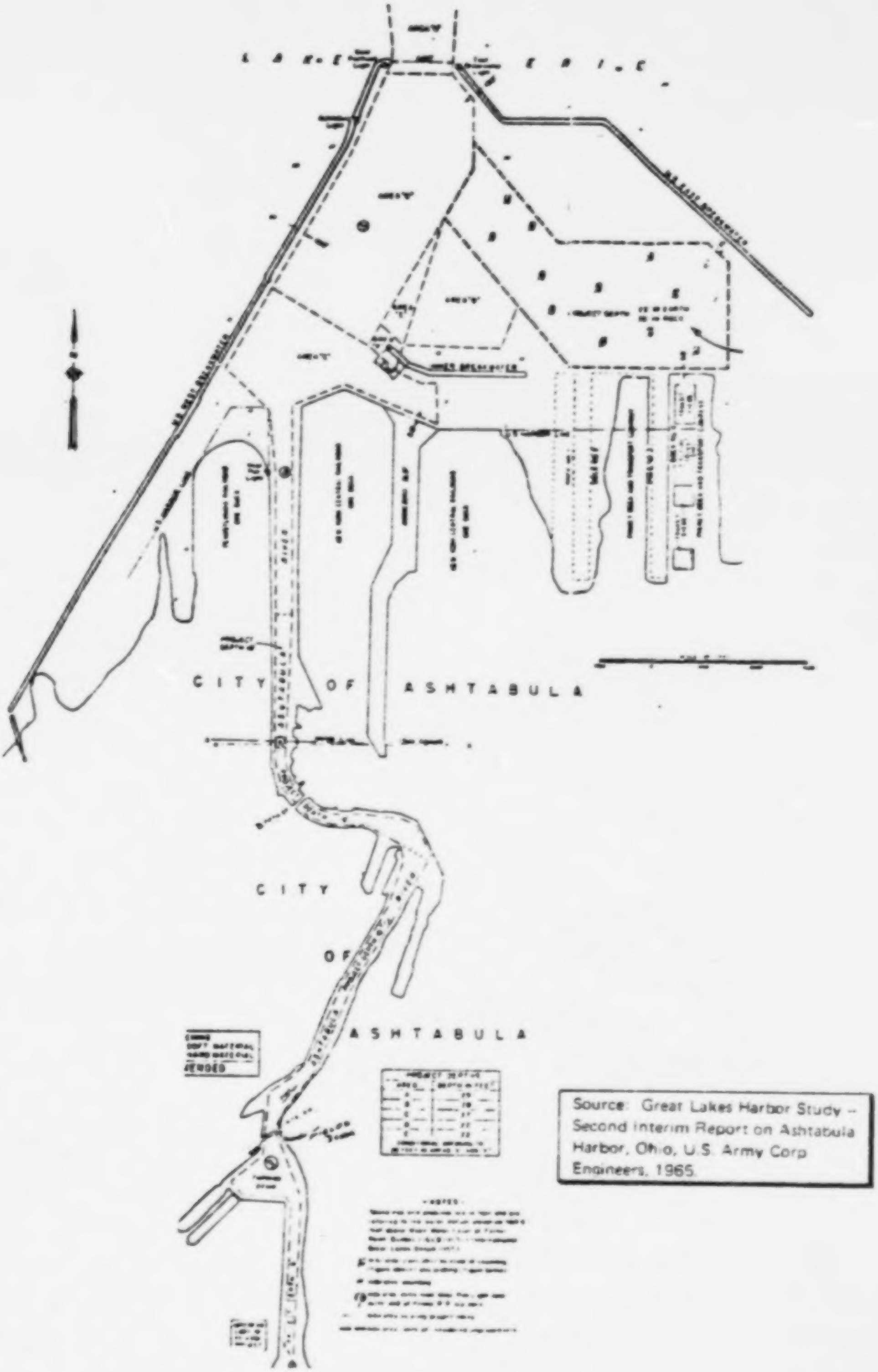
The primary purpose of this section is to present available historical information on the Ashtabula River, Harbor and adjacent Lake Erie areas as they relate to the present study. No attempt has been made to draw conclusions as to the historical changes in Lake Erie or to survey lake conditions as a whole. Recent papers presenting useful discussions of changes in fish populations caused by overfishing (Regier et al, 1969) and changes in lake-wide water quality (Beeton and Edmondson, 1972) have been presented, but relatively little specific data concerning the Ashtabula Harbor area is available.

Physical and Chemical Properties

The Ashtabula River Basin encompasses some 137 square miles. Based on commerce and total tonnage of all commodities shipped through Ashtabula Harbor, the harbor is an important deep draft, inland commercial port. Net tonnages of major commodities shipped were in excess of 11 million tons in 1971 with a substantial increase in shipping experienced between 1966 and 1971.

Average flow for the Ashtabula River is approximately 169 cubic feet per second into Lake Erie; dry weather flow is normally around 10 cfs and decreases to zero occasionally (Vol. 4, ACE 1968 Report). During the period 1-16 September 1973 daily flow averaged approximately 1.5 cfs (Refer to Table 1).

The outer harbor of Ashtabula Ohio, encompasses 185 acres, while the inner harbor extends approximately two miles up the Ashtabula River. The outer harbor is enclosed by two breakwaters: the western (7,780 ft. long) and the eastern (4,400 ft. long) breakwaters (See Figure 1).


LAKE ERIE
CITY OF ASHTABULA
CITY OF ASHTABULA

Source: Great Lakes Harbor Study – Second Interim Report on Ashtabula Harbor, Ohio, U.S. Army Corp Engineers, 1965.

Figure 1 ASTABULA HARBOR AREA

Table 1
SUMMARY OF LOW FLOW DISCHARGE DURING SEPTEMBER 1-16, 1973*

Date	Discharge (cfs)
Sept. 1	1.5
2	1.1
3	0.9
4	0.7
5	0.6
6	4.0
7	3.5
8	2.8
9	1.8
10	1.3
11	1.1
12	1.0
13	0.81
14	0.81
15	0.81
16	0.73

Of the 24 major tributaries flowing into Lake Erie, the Ashtabula River (Lake Erie Report, 1968) has the:

1) smallest drainage area (137 mi^2)
2) lowest average flow (169 cfs)
3) lowest recorded 7 day low flow (0.0 cfs)
4) fifth highest percent runoff from precipitation (45%)

---

*Coincides with sampling period - Task II, this study. Source: U.S. Geological Survey Water Resources Division, Columbus, Ohio

The small drainage area is reflected in the rather low average flow. Based on dilution potential alone, the Ashtabula is the least able to handle large volumes of oxygen demanding wastes. Steep terrain and soil characteristics convert a high percentage of the precipitation into runoff water.

Only 0.072% of the total water supply to Lake Erie is provided by the Ashtabula. The pollutant load based on 1967 figures is shown in Table 2.

In an attempt to place the Ashtabula River in perspective, Table 3 was constructed to compare six major tributaries of the Lake Erie Central Basin as to their BOD_5, total solids, and chloride content. This comparison illustrates that the Ashtabula River contributes the lowest pollutant load of any of the rivers for which calculations were made. This indicates that, even though the Ashtabula has the lowest annual average discharge, it also has the lowest pollutant load. This observation, however, can be misleading unless additional data are examined. A case in point is the data for annual minimum flow and data for the Ashtabula River obtained by the U. S. Geological Survey. Minimum flow as provided by the Lake Erie Report (1968) is 0.0 cfs and the 7-day Low Flow (10 year recurrence) is 0.0 cfs at the mouth. Of all significant U. S. tributaries to Lake Erie, the Ashtabula has the lowest minimum flow and is the only one which has a value of 0.0 cfs for the 7-day Low Flow (10 yr.).

The annual minimum commonly occurs during late August and September, a condition which creates conditions in which essentially the only flow recorded in the river is waste effluent from the Ashtabula industrial complex.

Enlargement of harbor areas near the mouth of the river has significantly reduced stream velocities and thus increased the need for expanded dredging operations. Dredgings, totalling over 345,000 yd^3 were removed from the

Table 2

ASHTABULA WASTE DISCHARGES TO LAKE ERIE 1966-67 (SHORT TONS/YR.)

PARAMETER (short tons/yr)

	BOD_5	SOLIDS		Total Nitrogen (N)	Total Phosphorous (P)	Chlorides
		Total	Susp.			
Ashtabula River	200	24,600	4,600	100	14	2800
Lake Erie Totals	159,480	39,417,213	4,536,548	167,835	27,342	4,449,646
% Ashtabula Contribution	0.13%	0.06%	0.10%	0.06%	0.05%	0.06%

Source: Pollution of Lake, Erie, Lake Ontario, and the International Section of the St. Lawrence River, Vol. 2, Report to the International Joint Commission, 1969.

Table 3

TRIBUTARY WASTE DISCHARGES, FLOW AND CONCENTRATIONS LAKE ERIE 1966-67
(U.S. Central Basin Rivers)

RIVER	AVE FLOW		WASTE LOADING TOT. SOLIDS			WASTE LOADING BOD_5			WASTE LOADING CHLORIDES		
	cf/sec	cf/yr	short-ton/yr	lb/yr	poll. conc. lb/ft^3	short-ton/yr	lb/yr	poll. conc. lb/ft^3	short-ton/yr	lb/yr	Poll. conc. lb/ft^3
Ashtabula	169	$5.33x10^9$	24,600	$0.05x10^9$	0.0092	200	$4x10^5$	$0.75x10^{-4}$	2800	$0.056x10^8$	10.5×10^{-4}
Conneaut Ck.	257	$8.10x10^9$	45,100	$0.09x10^9$	0.011	400	$8x10^5$	$0.99x10^{-4}$	5700	$0.114x10^8$	14.1×10^{-4}
Grand R.	784	$24.72x10^9$	1,510,000	$3.02x10^9$	0.122	1300	$26x10^5$	$1.05x10^{-4}$	680,000	$13.6x10^8$	550×10^{-4}
Cuyahoga	850	$26.8x10^9$	509,000	$1.02x10^9$	0.038	8900	$178x10^5$	$6.64x10^{-4}$	79,000	$1.58x10^8$	60×10^{-4}
Vermillion	228	$7.19x10^9$	90,000	$0.18x10^9$	0.025	200	4×10^5	$0.56x10^{-4}$	4,400	$0.088x10^8$	12.2×10^{-4}
Rocky R.	273	$8.61x10^9$	160,000	$0.32x10^9$	0.037	1400	$28x10^5$	$3.25x10^{-4}$	21,000	$0.42x10^8$	48.8×10^{-4}

harbor in 1968 (ACE Report, 1968). Local reports indicate that in recent years no dredging has been done up river from the 5th St. Bridge, approximately 0.7 miles from the river mouth.

As mentioned before, sluggish flows, particularly prevalent in late summer and fall, greatly increase sedimentation near the mouth of the river with a resultant lowering of water quality in the harbor. The time of travel in dredged channels has been estimated to be a week or more (FWPCA, 1968).

Flushing Time in Ashtabula Harbor

Flushing time in Ashtabula Harbor is extremely variable, depending on:

1) Volume of flow from the river
2) Volume of water in the harbor
3) Circulation patterns within the harbor
4) Effluent wastewater volume

Results of sampling in the ACE (1968) study indicate that most of the river flow is discharged through the northern breakwater opening while small amounts are discharged through the shallow opening in the east breakwater near shore.

Flushing time for the harbor was computed for the period 9-11 May 1967. During this period, the average flow of the river was 586 cfs (more than three times the average annual flow). The sodium ion was chosen as a tracer for the river water distribution in the harbor because it is not readily removed by chemical precipitation or biological uptake in this environment.

Analysis of sodium in the open lake yielded an average value of 13.5 mg/l selected as a background value. Harbor samples analyzed enabled selection of 21.0 mg/l as a representative sodium concentration. Samples taken 3/8 mile upstream from the mouth of the river had a mean concentration of 30.6 mg/l.

The percent volume of river water (V_r) present in the harbor during this period was determined using the relationship:

$$V_r S_r + V_n S_n = (V_r + V_n) S_o$$

where: S_o = sodium concentration in harbor

S_n = sodium conc. in lake

S_r = sodium conc. in river

V_n = % lake water in harbor

V_r = % river water in harbor

since $V_n = (100-V_r)$

solving: $V_r S_r + (100-V_r) S_n = (V_r + 100-V_r) S_o$

$$V_r S_r + 100 S_n - V_r S_n = 100 S_o$$

$$V_r S_r - V_r S_n = 100 S_o - 100 S_n$$

$$V_r (S_r - S_n) = 100 (S_o - S_n)$$

$$V_r = \frac{100 (S_o - S_n)}{S_r - S_n}$$

$$V_r = \frac{100 (21.0 - 13.5)}{(30.6 - 13.5)} = \frac{100 (7.5)}{17.1} = 43.86 = 44\%$$

Therefore, 44% of the water in the harbor was river water according to this calculation.

Total volume of water in the harbor was determined in the Army Corps of Engineers study by dividing the harbor into zones of equal depth and determining the area of each depth by planimeter. The area times the average depth equals the volume at L.W.D. or 294,270 X 10^3 cubic feet. The total volume of the harbor at L.W.D. + 2.3 ft. (the value at the time of the measurements) is 327,321 X 10^3 cubic feet. Average daily river inflow into the harbor was 50,630 X 10^3 cubic feet.

Flushing time was then computed from the relationship:

$$\text{Flushing time} = \frac{V_r}{Q} = \frac{143{,}367 \times 10^3 \text{ cubic feet}}{50{,}630 \times 10^3 \text{ cu. ft./day}}$$

where V_r = 43.86%(from above) of 327,321 X 10^3 cu. ft.

or 143,367 X 10^3 cu. ft.

Q = discharge (daily river inflow)

Assuming a flow of river discharge along a path 1200 feet wide from the river mouth to the harbor entrance, and further assuming that 80% of the river flow followed this path, the Path Flushing Time was calculated at 29.8 hours (ACE, 1968) under the flow conditions at that time (higher than average flow).

From the analysis performed in Ashtabula Harbor, it is apparent that flushing time calculations cannot be generalized in these circumstances because of several factors:

1) lake levels
2) wind direction and set-up

3) river discharge
4) presence of "dead spots" on the bottom

Further, this technique is difficult to evaluate because it is not known where the discharge values were taken, i.e., gaging station upstream or at the river downstream of several additional outfalls, particularly Fields Brook.

Since the Ashtabula River discharge decreases to nearly zero during low flow periods, the technique used in the Army Corps of Engineers report would be difficult to apply unless simultaneously the following parameters are known:

1) Concentration of sodium in the river, harbor and lake.
2) Discharge including river (upstream) Fields Brook and other contributors.

Data examined from the STORET system was inadequate to attempt to construct a profile of values for different discharge conditions. These data, particularly low flow flushing times, would be valuable as indicators of "worst case" conditions existing in the waterway.

Dispersion of Pollutants in Lake

Mixing patterns of tributary discharges with lake water are extremely important if the net effect of pollutants released is to be determined (FWPCA, 1968). The following are important considerations in determining mixing patterns:

1) thermal structure
2) bottom and shoreline topography
3) prevailing winds
4) longshore currents

Generally speaking, tributary discharges on the southern shore tend to stay near shore and move eastward primarily as a result of the prevailing south westerly winds during the spring and summer. However, in the fall and early winter, similar discharges may under-run the lake water and be distributed over the entire basin (p. 75, FWPCA, 1968). Temperature differences, however, may override density differences due to dissolved solids in allowing river water to flow over lake water (p. 51, FWPCA, 1968).

The fact that the Ashtabula River exerts an important influence on Lake Erie was found in a study by the Department of Health, Education, and Welfare (1965). As evidenced by coliform counts in the HEW study, the river exerted an influence on Lake Erie water quality 1.5 miles from the mouth during flow of 5.1 cfs (low flow). Higher flows should create a greater sphere of influence and thus seasonal variations in river water quality, as well as Lake Erie water quality in the vicinity of the harbor. Distribution of several measured parameters lakeward from the harbor area suggests that increased river discharge combined with the predominant eastward current flow of the lake produces a significant influence that may extend for 2-3 miles or more from the harbor entrance, at least during peak flow (ACE, 1968).

Former practices for discharging dredged materials offshore in the Ashtabula area could detract from water quality if they were to be continued. The discharge of dredged materials on the Canadian side of Lake Erie takes place in deeper waters and further offshore because Canadian regulations require dredging contractors to dispose of dredging spoils in "water no less than 15 meters (50 ft.) nor within three miles of dredging site" unless faced with unusual conditions (IJC, 1969). Most dredgings from Ashtabula have previously been discharged in an area two miles or less northeast of the harbor entrance (ACE, 1968). Therefore, aggravation of the existing situation may take place during dredging and dredge disposal. Current U.S. Army Corps of Engineer plans call for construction of a diked disposal site on the outside of the west breakwater. At the time of preparation of this report, construction of the site had not begun. Dredging has not been performed in Ashtabula Harbor in the past two years.

The Aquatic Community at Ashtabula, Ohio

Plankton - A search for literature pertaining to the phytoplankton of the Ashtabula River yielded very little specific information. A 1950-51 survey (State of Ohio, 1953) inspected the phytoplankton and benthos in Ashtabula Harbor, as well as toxic effects of river water on *Daphnia magna*, a cladoceran zooplankton (Class Crustacea, Phylum Arthropoda). Poppin (State of Ohio, 1953) found only one of fourteen samples of river water, which was obtained from the Ashtabula Harbor bridge (probably the 5th St. bridge) to be toxic to *Daphnia*; 50 percent were immobilized in 96 hours. Sullivan (State of Ohio, 1953) identified phytoplankton collected from the mouth of the Ashtabula River. Samples of water from the lake, river mouth, and upstream (probably ≈ 0.7 miles) had phytoplankton concentrations of 8.48, 4.27 and 3.02 X 10^8 μ^3, respectively.

Lake water in the area contained the diatoms *Melosira*, *Stephanodiscus*, *Fragilaria*, and *Asterionella* in order of dominance. Water samples obtained from the harbor yielded the same plankters in the same order of dominance, a phenomenon explained by Sullivan to be due to influx and mixing of lake water and river water.

Phytoplankton - Lake Erie phytoplankton exhibit classical vernal and autumnal phytoplankton maxima, separated by winter and summer minimum. Spring maximum exceeds the fall maximum in abundance of phytoplankton, but usually lasts for a shorter time. Davis (1964) has shown that over the years at Cleveland there is a consistent lengthening and intensification of fall and spring maxima, and a shortening of summer and winter minima. Table 4 gives average phytoplankton populations for the Central Basin of Lake Erie.

Davis (1962) summarized literature concerning dominance in the three major basins. All investigators agree on dominance of diatoms in winter and spring except Verduin (1960) who listed green phytoflagellate *Chlamydomonas* as an important item in addition to the diatoms.

Table 4

AVERAGE PHYTOPLANKTON POPULATIONS OF THE CENTRAL BASIN OF LAKE ERIE
(ORGANISMS PER ml, CLEVELAND PROGRAM OFFICE DATA, FWPCA, 1968)

Type of Algae	Season	Abundance (# of Org/ml)
Diatom	Spring	238
Blue-green	"	91
Green	"	81
Flagellate	"	51
Total	"	461
Diatom	Summer	45
Blue-green	"	101
Green	"	137
Flagellate	"	32
Total	"	315
Diatom	Fall	284
Blue-green	"	12
Green	"	180
Flagellate	"	28
Total	"	504
Diatom	Winter	391*
Blue-Green	"	20*
Green	"	177*
Flagellate	"	58*
Total	"	646*

* Data averaged from all stations.

Studies of plankton from the years 1928-1951 also showed a summer dominance of diatoms, occasionally along with chrysophyte phytoflagelate Dinobryon. Davis (1962) and Verduin (1960) showed that Ceratium hirundinella, phytoflagellates, and Pediastrum to be of great importance, sometimes along with diatoms, sometimes without them. In many studies, fall months have shown a tendency to have larger quantities of green and blue-green algae, usually with admixture of diatoms.

Davis (1964, 1965) has shown that the total quantity of the phytoplankton in the central basin of Lake Erie has increased steadily over the years, according to records taken by the Cleveland Division of Water and Heat. In daily records for 13 of the years between 1919-1934 counts exceeding 4 X 10^6 cells/liter occurred twice, whereas counts of in excess of this number occurred in all but one of the 19 yrs for which records are available between 1934-1964. Average years for which data were available indicated a regular increase from a low of 81,000 cells per liter in 1928 to 2,423,000 cells per liter in 1962 and 2,378,000 per liter in 1964. Davis (1965) showed that between 1927-1964 the annual average of the phytoplankton increased at a mean rate of 44.3 cells/ml/yr, but between 1956-1964 the mean rate had increased to 122.0 cells/ml/yr. These rates and totals were thought to be an indication of rapid and increasing eutrophication of the lake, sped undoubtedly by enrichment with domestic, industrial, and agricultural wastes.

Zooplankton. The zooplankton in the Great Lakes have been studied quantitatively but much less than the phytoplankton. As with the phytoplankton, historically more studies have been undertaken in Lake Erie than in the other Great Lakes (Davis, 1966), although recent work indicates that this trend has changed.

Protozoans have formed only a minor portion of the total zooplankton as a rule. Burkholder (1960) found Vorticella attached mainly to colonies of Anabaena to be the most abundant, with Difflugia common in the eastern and central basins 1928-30. Chandler (1940) listed in addition Codonella cratera as common in the warm months of 1939. Davis (1954b) described Vorticella and Codonella as the most common and regular of the protozoans in the Cleveland Harbor area in 1950-51 with Tintinnidium also common at times; Codonella became very abundant in the summer and fall of 1951, the mid summer maximum containing an average of 248 per liter. On September 30, 1951, Codonella dominated the zooplankton with an average of 1,130 per liter, and in one sample there were 3,500 per liter.

Rotifers tend to be abundant in the spring and the fall in central Lake Erie studies. The most abundant rotifer species in all of the studies included Polyarthra sp., Keratelia cochlearis (Burkholder, 1929 a, b, 1960; Ahlstrom, 1934; Chandler, 1940; Davis, 1954, 1962; Williams, 1962).

In addition, Burkholder found Chromogaster ovalis to be abundant at times, as did Ahlstrom (1934) for Synchaeta sp., Filinia longiseta and Brachionus angularis; Chandler (1940) for Synchaeta; Davis (1954), for Synchaeta sp; Davis (1962) for Conochilus unicornis.

Three-seasonal quantitative studies of Lake Erie zooplankton have shown both summer and autumnal maxima of the Cladocera, a judgment supported by Wright (1955). In studies by Davis (1954, 1962), the summer cladoceran maximum occurred in June and coincided with the extremes of the phytoplankton minimum. According to Davis (1966), the genus Daphnia has been the most important, both because of size and abundance. Several authors have listed Daphnia retrocurva as the most abundant daphnid in Lake Erie (Davis, 1954, 1962; Bradshaw, 1964; Bigelow 1972).

Of non-daphnid cladoceran genera, Diaphanosoma, Bosmina, and Leptodora are most frequently listed as common or abundant (Davis, 1966).

The calanoid copepods that have been listed regularly for Lake Erie consist of five or six species of Diaptomus, one of Epischura, and one of Limnocalanus. The most abundant calanoids have been the diaptomids particularly Diaptomus ashlaudi, D. oregonesis and D. siciloides (Davis, 1966).

Several studies have shown that Diaptomus siciloides was rare in 1928-30, present but limited in 1939, but by 1946-47 in the western basin and 1956-57 in the central basin, common during the warm months in all three basins. This development is considered significant because it is an indication of fundamental changes in the lake itself. D. siciloides is known primarily as an inhabitant of ponds and warm eutrophic waters (Davis, 1966).

Macrofauna

According to Henson (1966), the Great Lakes have the following approximate number of species of major animal groups:

Taxon	No. of Species in the Great Lakes
Porifera	2
Oligochaeta	10
Turbellaria	10
Ostracoda	11
Isopoda	3
Amphipoda	7
Gastropoda	60
Pisidium (Pelecypoda)	17
Sphaerium (Pelecypoda)	10

Benthic fauna reported present for Lake Erie (Henson, 1966 ; Carr and Hiltunen, 1965).

Crustacea	Pontoporeia Gammarus Hyalella Asellus Mysis relicta

Insecta

- *Hexagenia*
- *Ephemera*
- *Ephoron*
- *Oecetis*
- *Procladius*
- *Coclotanypus*
- *Cryptochironomus*
- *Tendipes*

Pelecypoda

- *Sphaerium* (4 species:
  - *S. corneum*
  - *S. occidentale*
  - *S. striatinum*
  - *S. transversum*)
  - *S. lacustre*
- *Pisidium* (7 species:
  - *P. amnicum*
  - *P. casertanum*
  - *P. compressum*
  - *P. henslowanum*
  - *P. nitidum*
  - *P. punctatum*
  - *P. subtruncatum*
- *Lampsilis*
- *Anodonta*
- *Elliptio*

Gastropoda

- *Amnicola*
- *Bithinia*
- *Campeloma*
- *Goniobasis*
- *Heliosoma*
- *Physa*
- *Pleurocera*
- *Somatogyrus*
- *Stagnicola*
- *Valvata*
- *Bulimus*

Tables 5 and 6 provide a breakdown of benthic fauna found in the Ashtabula River (stations 18, 19), harbor (20, 21, 22, 23) and lake dredging disposal site (station 9 encircled by stations 1-8). It is interesting to note that the pollution sensitive mayfly larvae (*Hexagenia* sp.) were found at a few stations in mid-lake of the central basin but only at one station (northeast of Ashtabula off the southern shore in a 1963-64 study (FWPCA, 1968).

Brown (State of Ohio, 1953) investigated the benthos of Ashtabula Harbor in 1950-1951. He described the bottom sediment as "organically rich, dark colored muds". Brown reported 210 tubificids for 36 in^2 of sediment. Of ten rivers studied, only the Maumee and Black River sediments contained higher amounts of tubificids. Genera isolated from the Ashtabula Harbor sediments were:

Chironimidae (midge larvae)
*Elmis** (beetle larvae)
Herpobdellidae (leeches)
Musculium transversum (Mollusca)
Pisidium sp. (Mollusca)
Tubifex sp (Tubificidae, Oligochaeta)
Limnodrilus sp (Tubificidae, Oligochaeta)

During Spring 1967, two harbor stations were sampled for benthic fauna at Ashtabula (ACE, 1968). In all samples from the lake, harbor and river, Oligochaetes (Family Tubificidae) were the dominant organisms. The Tubificid species *Peloscolex multisetosis* (Smith) was reported in all samples and averaged 0.7% of river Tubificids, 1% of harbor, and 4-6% of spoil dump-ground Tubificids. Examination of the study data indicate that the harbor samples had the lowest variety of organisms with mollusca and *Chironomus* (midge larvae) as the only significant organisms present in addition to Tubificids.

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* Misclassified, *Elmis* is actually a European genus not found in the Great Lakes.

Table 5

BENTHIC FAUNA IN RIVER AND HARBOR AT ASHTABULA, OHIO

ORDER GENUS SPECIES	OLIGOCHAETA (TUBIFICIDS) EXCL. PELOSCOLEX	OLIGOCHAETA PELOSCOLEX MULTISETOSUS	HIRUDINEA GLOSSIPHONIA HETEROCLITA	HETERODONTA PISIDIUM SP.	HETERODONTA MUSCULIUM SP.	HETERODONTA SPHAERIUM SP.	MESOGASTROPODA AMNICOLA LIMNOSA	MESOGASTROPODA VALVATA SP.	MESOGASTROPODA BITHINIA TENTACULATA	DIPTERA CHIRONOMUS SP.	DIPTERA CHRYSOGASTER SP.	REMARKS
CRUISE AND STATION	INDIVIDUALS PER SQUARE METER OF BOTTOM											
RIVER A6701-18	1425	25										Tubificids dark in color
RIVER A6701-19	5625	25		25								"
HARBOR A6701-20	2775	25			25					50		"
HARBOR A6702-20	6775	75		25							25	"
HARBOR A6701-21	15000	25		25								"
HARBOR A6701-22	25000	300	25	100			50		25	75		"
HARBOR A6702-23	13900	525		50	25	50		DEAD ONLY		225		"

SOURCE: Dredging and Water Quality Problems in the Great Lakes, Vol. 4, U. S. Army Corp Engineers (1968).

Table 6

BENTHIC FAUNA AT DISPOSAL SITE, ASHTABULA, OHIO

ORDER GENUS SPECIES	OLIGOCHAETA (TUBIFICIDS) EXCL. PELOSCOLEX	OLIGOCHAETA PELOSCOLEX MULTISETOSUS	HIRUDINEA HELOBDELLA STAGNALIS	HIRUDINEA HELODDELLA FUSCA	NEMATODA	HETERODONTA PISIDIUM SP.	HETERODONTA MUSCULIUM SP.	HETERODONTA SPHAERIUM SP.	ISOPODA ASELLUS SP.	MESOGASTROPODA AMNICOLA LIMNOSA	MESOGASTROPODA BITHINIA TENTACULATA	MESOGASTROPODA VALVATA SP.	MESOGASTROPODA VALVATA TRICARINATA	DIPTERA CHIRONOMUS SP.	REMARKS
CRUISE AND STATION	INDIVIDUALS PER SQUARE METER OF BOTTOM														
A6702-01	1650					50									
A6709-01	2375	75	25			200								25	
A6702-02	2025	225	25			250		50	75	25				175	
A6702-03	5425	175			175	375								375	+25 Amnicola Sp?
A6702-04	7425	350			25	325	25	75		125				225	
A6702-05	8800	275	25		150	375		50		50	50	100	75	425	
A6703-06	1950	25		25			25							100	
A6709-06	2525	200			100	125	25			25	50			275	
A6703-07	3175	300	75		50	100		25		25	25			225	+25 Amnicola?
A6709-07	1700		50											100	
A6703-08	3550	50			175	125	25		25				25	575	
A6709-08	6025	550	50	100	250	250	50					50		450	
A6702-09	1475					50						25			Slope location sand bottom
A6709-09	800					50									Slope location sand bottom

SOURCE: Dredging and Water Quality Problems in the Great Lakes, Vol. 4, U. S. Army Corps Engineers (1968).

There has been relatively little attention to macroinvertebrates in Lake Erie and tributary streams. Some attention, at least in terms of noting the population characteristics of bivalves and crayfish, should be given. Other invertebrates, e.g., *Eurytemora affinis*, a euryhaline copepod, are now apparently established in Lake Erie and harbors (Eugel, 1962), but no quantitative information is available.

The 1967 U. S. Lake Survey (ACE, 1968) also included a study of the macrofauna in the Ashtabula River and Harbor.

Organisms were collected and identified at two stations in the river, five in the harbor, and nine in the lake "dumping ground".

Organisms which were found in the river and harbor stations included:

-- Oligochaetes (Family Tubificidae)

-- Molluscs

-- *Chironomus* (midge larvae)

Organisms which were found in the macrofauna of the lake include:

Oligochaetes
Sphaerids
Gastropods
Chironomus (*tendipes* sp.)
Leeches (*Helobdella stagnalis*, *H. fusca*)
Nematodes

It was concluded by the ACE (1968) study that judging from the number of variety of fauna present that the Ashtabula river samples indicated a polluted environment. For example, the only living organism other than the pollution tolerant Tubificids (sludge worms) found in the river sediment consisted of one sphaerid clam (genus Pisidium). Tubificids found on the river bottom were much darker in color and twice as large (1") as those found in the open lake. In contrast to the river, stations in the harbor exhibited populations of 25,000 individuals/m^2 and also exhibited a greater variety of organisms. All harbor stations had sphaeriid clams, although a station at the mouth of the river appeared to have much fewer individuals than all other harbor locations.

Recent Data - The dominance of diatoms during cooler months and of green algae in summer at Lake Erie water intakes located at Ashtabula, Ohio, was established during a five-year study (Reitz, 1973). Phytoplankton at Ashtabula, as well as other Lake Erie intakes, have decreased in abundance during the 1968-1972 investigations. Tables 7 and 8, taken from the Ohio EPA report show the annual phytoplankton standing crop for 1968-1972. Table 8 compares average yearly phytoplankton of nine areas in Lake Erie. Green algae dominance began as early as June and persisted as late as November. Dilution of plankton concentrations by rising Lake Erie waters could account for the reduction in cell numbers. However, decreases in enrichment of the water may also explain the reversal in eutrophic conditions. Low cell numbers as reported by the Ohio EPA and as noted in this study may attest to the effect of industrial discharges on nearshore and harbor areas like Ashtabula.

Sediment within a 1000 ft radius of the water intake was grey-brown sand, silt, and gravel. Biota included tubificids, sphaerids, amphipods, chironomids, ephemeropterans, prosobranchids, pulmonatans, hydra, and Bryozans.

Pollution Indicators - A dependable index for the classification of the extent of pollution has not emerged yet. Many have used the types of phytoplankton present to evaluate the eutrophication of a water body. (Davis, 1964; Williams, 1972; Meyer, 1971). Others have considered a tubificid dominance to be indicative of organic pollution (Brinkhurst and Jamieson, 1971; Aston, 1973). The percentage of Limnodrilus hoffmeisteri

Table 7

Phytoplankton standing crops and percent dominant group. (Values represent number of cells per 100 ml.) Code for % abundance is as follows: D = diatoms, BG = Bluegreen, G = Green, Fl = Green flagellate, FLO = Flagellate (others).

Station—Ashtabula

Month	1968	% abund	1969	% abund	1970	% abund	1971	% abund	1972	% abund
Jan.			166	61D	1080	100D			160	58D
Feb			582	82D	1282	92D	45	40D	85	84D
Mar.	3784	94D	3015	93D					280	98D
Apr.	5278	84D	1010	74D			1310	100D	447	99D
May	1193	59D	577	76D			356	46D	246	72D
June	295	43G	81	50G	36	75G	136	60D	134	60G
July	520	69G	323	79D	163	39G	377	76G	138	80D
Aug.	410	31G	341	61G	504	68BG	320	46D	100	82G
Sept	325	73G	490	59G	328	66G	183	35D	212	70G
Oct	538	64G	360	47D	236	35D	680	68D	291	42D
Nov	208	55G	247	50D			247	52D	285	47D
Dec.	205	68D	548	71D	219	60D	378	60D	82	56D

Source: Distribution of Phytoplankton and Coliform Bacteria in Lake Erie, Ohio Environmental Protection Agency, March 1973

Table 8

Yearly phytoplankton averages. Values represent the # phytoplankters/100 ml.

Station	1968[1]	1969	1970[2]	1971[3]	1972
Toledo	4,870	2,155	1,198	2,070	513
Port Clinton	6,822	2,956	1,820	1,474	1,079
Sandusky	1,970	1,093	1,022	1,891	1,142
Vermilion	1,358	856	755	609	582
Cleveland Crown	1,059	449	666	476	364
Lorain	15,554	686	788	673	565
Cleveland Division	965	395	558	333	404
Cleveland Eastlake		588	570	1,070	312
Painesville	1,739	728	902	703	320
Ashtabula	1,276	645	481	403	205

1. January, February missing
2. March, April, May, November missing
3. January, March, June missing

Source: **Distribution of Phytoplankton and Coliform Bacteria in Lake Erie, Ohio Environmental Protection Agency, March 1973**

(common Oligochaete) in relation to the total number of oligochaetes may be a very useful guide to the degree of organic pollution in a locality (Brinkhurst, 1967; 1969). In grossly polluted situations, the number of oligochaetes stays high with representatives of other groups absent or scarce. The central basin of Lake Erie is dominated by *Peloscolex ferox*, a different species but same genus, found in river sediment samples from the Ashtabula River. Species of oligochaetes appear to be characteristic of pollution levels as well as temperature to some extent.

Heavy sewage and organic pollution are often associated with high numbers of *Tubifex tubifex* and *Limnodrilus hoffmeisteri*. These organisms are able to adapt their respiration to withstand low oxygen concentrations, or even anaerobic conditions for up to four weeks (Aston, 1973). *L. Hoffmeisteri* is able to reproduce under very low oxygen conditions as well.

Diatom community structure has been accepted by Williams (1972) and others as indicative of water quality. These less obvious organisms show high diversity in cleaner waters, and high numbers of a few common, tolerant species under conditions of pollution. They are easily identified by the wall structures and readily available in plankton samples.

Prominent species of the clam, *Pisidium*, are little known as to their depth, temperature or pollution dependence, although twice as many species are found in Lake Erie as in Lake Ontario. According to Brinkhurst (1969), the trend and tolerance of these fresh water clams might be very useful indicators to environmental conditions.

Coliform - In addition to the coliform counts available in the STORET system, information in the ACE Dredging Report (1968) indicates that the normal lake background of coliform bacteria varies but usually averages about 100/100 ml. About one and one-half miles from the Ashtabula River, values were 150/100 ml in 1964 (HEW, 1965). Total coliform counts near the city water intakes averaged approximately 250 and 490 organisms per 100 ml for 1971 and 1970 for the data examined here (EPA, 1972, 1971). East of the City's sewage treatment plant a count of 920/100 ml was obtained in 1968.

Dumping of dredged material from the river and harbor in the past has not aided the situation and at least raised the count during the short term the samples were taken. Scarce et al. (1964) showed that coliform can persist in the vicinity of dumping areas for some time.

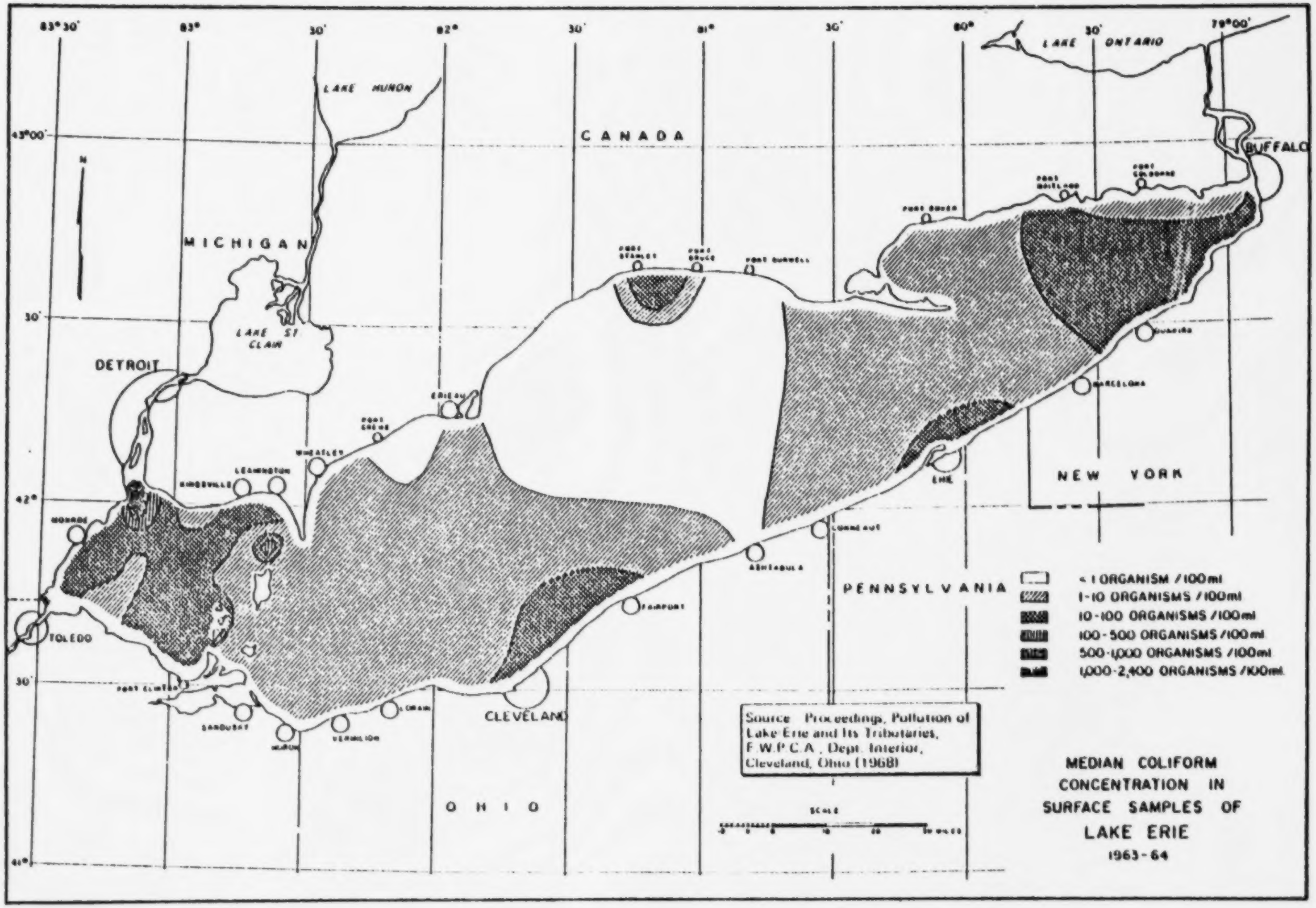
Figure 2 illustrates median coliform concentration in surface samples in Lake Erie 1963-64. An interesting pattern emerges showing a vast area in the central basin where median values of total coliform are less than 1 organism per 100 ml while it has been reported that median values of total coliform levels in the mouth of the Ashtabula River and harbor have exceeded 1000 organisms per 100 ml (FWPCA, 1968).

To illustrate coliform data available for the Ashtabula area, sample STORET data for the period 1963-1964 is shown in Table 9.

Table 9

STORET COLIFORM DATA (1963-1964)

STORET STATION	MILE PT.	DATE	MEAN TOT. COLIFORM/ 100 ml	FEC. COLIFORM MFM-FCBR/100 ml
380142	3.3	1/8/64-11/25/64	9998	
		4/15/64-11/25/64		1537
380141	2.3	1/8/64	9500	
380137	0.70	10/16/63-11/25/64	74,637	
		4/15/64-11/25/64		32894
380136	0.0	10/16/63-10/28/64	8073	
		4/30/64-10/28/64		


83°30'
83°
30'
82°
30'
81°
30'
80°
30'
79°00'
43°00'
30'
42°
30'
41°
N
LAKE HURON
LAKE ONTARIO
CANADA
MICHIGAN
LAKE ST CLAIR
DETROIT
TOLEDO
MONROE
KINGSVILLE
LEAMINGTON
WHEATLEY
ERIEAU
PORT STANLEY
PORT BRUCE
PORT BURWELL
PORT ROWAN
PORT MAITLAND
PORT COLBORNE
BUFFALO
DUNKIRK
BARCELONA
NEW YORK
ERIE
CONNEAUT
ASHTABULA
PENNSYLVANIA
FAIRPORT
CLEVELAND
LORAIN
VERMILION
HURON
SANDUSKY
PORT CLINTON
OHIO
SCALE
< 1 ORGANISM / 100ml
1-10 ORGANISMS / 100ml
10-100 ORGANISMS / 100ml
100-500 ORGANISMS / 100ml
500-1,000 ORGANISMS / 100ml
1,000-2,400 ORGANISMS / 100ml
MEDIAN COLIFORM CONCENTRATION IN SURFACE SAMPLES OF LAKE ERIE
1963-64

Source Proceedings, Pollution of Lake Erie and Its Tributaries, F.W.P.C.A., Dept. Interior, Cleveland, Ohio (1968)

Figure 2 Median Coliform Concentration in Lake Erie (1963-1964)

Water Chemistry

Extensive literature research concerning the water quality of the study area turned up very little in the way of published articles with the following exceptions: STORET data, the ACE report (1968), IJC Report, V. 2 (1969) and the FWPCA Report (1968). Most of the published data concentrates on Ashtabula Harbor, the nearshore area, and the Central Basin of Lake Erie. The U.S.G.S. Water Resources Division headquartered in Columbus has installed a continuous flow analytical device which samples and provides analysis for temperature, conductivity, pH and dissolved oxygen. This sampling station is located at Jack's Automarine at approximately the 0.8 milepoint of the Ashtabula River.

Revised water quality standards for Ohio were adopted by order of the Director of the Ohio Environmental Protection Agency on 27 July 1973. On 9 August 1973, these standards were submitted to Francis T. Mayo, EPA Regional Administrator for approval. Standards were being revised again in late 1974. This is discussed under the heading, "Sampling Program", in Section 6 of this report.

The U. S. Lake Survey (ACE, 1968) surveyed water quality at several points in the Ashtabula area in 1967 during average discharge of 385 cfs. Although station depths were not given, it is probably safe to assume surface samples were taken. These data tend to be somewhat in agreement with other data except for conductivity. Table 10 lists parameters measured and their concentrations. All river sample stations (2) were located between mile point 0.8 and the mouth of the harbor. Other sample stations were located in the harbor and in Lake Erie (nearshore).

The Army Corps of Engineers Dredging Report also lists several harbors along Lake Erie and a table comparing Ashtabula Harbor to Erie, Fairport, Cleveland, Lorain, Sandusky and Maumee Harbors is included here (Table 11). The concentrations of most parameters are in agreement with previous work with the exception of conductivity and pH.

Table 10

1967 U. S. LAKE SURVEY STUDY

ASHTABULA RIVER

SAMPLING DATES: 9, 10, 11, 15, 16, 17 MAY 1967

RIVER DISCHARGE: low 120 cfs (5/15); Hi 780 cfs (5/11); AV. 385 cfs

mg/l (UNLESS OTHERWISE SPECIFIED)

Station	Location	pH[a]	D.O.	Tot.Alk[b]	Sp. Cond. (Micromhos)	Eh. (volts)	PO_4	NO_3	SO_4	Cl[c]	SiO_2	Ca	Mg	Na	K
18	River	RIVER/HARBOR 6.83-7.31 LAKE 8.06-8.11	RIVER/HARBOR 99-103% SAT. LAKE 99-100% SAT.	28	330	0.075	0.2	2.0	33.8	58.3	3.2	39.2	5.3	26.3	2.3
19	River			27	362	0.088	0.2	1.6	35.5	64.6	3.3	40.1	5.6	30.6	2.5
20	Harbor			66	355	0.085	0.2	2.7	34.5	43.1	1.0	41.4	7.2	20.2	2.2
21	"			50	345	0.083	0.2	2.0	35.8	49.6	2.1	40.4	6.4	22.5	2.5
22	"			59	347	0.108	0.2	2.5	33.7	44.4	1.7	41.2	6.9	21.8	2.4
23	"			--	--	--	0.1	1.9	36.5	--	1.5	42.1	7.0	21.8	2.0
24	"			64	355	0.076	0.2	1.7	34.0	43.6	1.0	40.4	6.7	20.5	1.2
25	Lake			94	--	0.126	0.0	2.4	29.5	--	--	41.8	8.8	15.6	1.4
26	"			--	--	--	0.0	--	--	--	--	--	--	--	--
38	"			92	--	0.086	--	2.0	32.5	--	--	40.6	8.6	13.5	1.0

a. Acidic water flowing from Fields Brook during this same time averaged 2.9.

b. Low alkalinity in river related to acidic discharges from Fields Brook.

c. -Cl range of 85-539 mg/l found in river between Fields Brook and station 19.

-Fields Brook ran 681-1854 mg/l.

-Upstream "background" levels ran 28-50 mg/l.

REFERENCE: Dredging and Water Quality Problems In The Great Lakes, Vol. 4 U. S. Army Corp Engineers, (1968).

Table 11

WATER QUALITY-NEARSHORE AND HARBORS

(mg/1 or μmhos/cm)

Parameter	Michigan waters of Lake Erie Min	Michigan waters of Lake Erie Max	Maumee Bay Min	Maumee Bay Max	Sandusky Bay Min	Sandusky Bay Max	Lorain Harbor Min	Lorain Harbor Max	Cleveland Harbor Min	Cleveland Harbor Max	Fairport Harbor Min	Fairport Harbor Max	Ashtabula Harbor Min	Ashtabula Harbor Max	Erie Harbor Min	Erie Harbor Max
Cond (25°C)			280	460	256	800	300	340	--		330	5920	--		330	360
DS			200	290	190	680	160	230	180	370	180	6000	170	230	180	290
TS			200	350	210	760	170	270	180	680	190	6100	180	250	200	290
Chlor.	27	82	20	32	16	32	19	25	14	88	--		24	42	26	38
Sol PO_4	.05	.20	.02	.19	.02	.17	.02	.11	--		--		.02	.06	.01	.03
SO_4			--		25	256	27	37	--		--		--		26	44
SiO_2			0.6	1.7	0.3	5.9	.40	1.10	--		--		--		.3	.5
K			1.4	2.6	1.2	4.0	1.3	2.2	--		--		--		1.4	1.9
Mg			12	18	10	38	9	11	--		--		--		9	9
Ca			35	42	38	114	34	38	--		--		--		42	47
Na			12	20	10	16	10	13	--		--		--		17	21
ABS	<.025		.05	.15	.05	.20	.05	.15	--		--		--		.07	.14
Alk	78	157	86	120	87	120	88	99	81	130	90	110	94	100	90	96
pH	8.4	9.2	7.4	9.7	7.5	9.1	7.5	8.7	6.7	9.5	7.1	8.7	8.2	8.5	7.3	8.1
Temp			21	25	23	26	24	25	16	21	23	29	15	17	16	19
DO%S			60	95	65	115	80	95	70	95	80	130	95	110	Avg.	60%
BOD			1.5	4.0	2.1	6.3	1.0	2.3	--		--		2.0	5.6	Avg.	3.3
COD			12	53	13	42	10	28	8	22	8	12	7	11	Avg.	24
Phenol	0.0	0.058	--		--		--		--				--			
Total N			.82	3.45	.82	3.50	.50	4.20	--						.66	.80
Org N	0.20	0.30	.07	1.33	.53	2.30	.01	1.10	--				.29	.49	.30	.59
Amm N	0.20	0.30	.30	1.80			.12	.90	--				.03	1.55	.12	.23
Nit N	0.11	0.91	.00	.80	.01	1.80	00	2.90	--						.07	.14

SOURCE: Dredging and Water Quality Problems of the Great Lakes, Vol. 4, U. S. Army Corp Engineers (1968)

Water Chemistry data compiled from the Cleveland Program Office of the then FWPCA (1968) in 1963-64 and 1967-68 are reprinted here for comparison (Table 12a, 12b). These tables give data for the Western, Central and Eastern Basins of Lake Erie. For purposes of this study, the values in the Central Basin are emphasized because the Ashtabula is a tributary of the Central Basin. With respect to every parameter except nitrate nitrogen (% change -44.4%), chlorides (-4.2%) and silica (-45.6%), the values of measured substances increased by 3-100 percent. Soluble phosphorous (ortho phosphate) increased the greatest (100 percent) over the four year period. The data are particularly important with respect to phosphorous which is usally listed as a limiting factor in algal growth.

The ACE study also compared several parameters measured during dredging to National Water Quality Standards (Table 13). These data, for the parameters measured (pH, DO, DS) indicate that surface waters were within applicable limits. Determinations of metals content, suspended solids, organic chemicals, etc. were not made however. Samples taken during dredging (new work) in Ashtabula Harbor were analyzed as part of this study. New work dredging effects are expected to be minor because of the nature of the material dredged.

The use of data contained in Tables 10,11,12 & 13 will serve as a benchmark for "background levels" to be compared with data obtained in this effort. It is important to note that almost all samples collected for the Lake Erie 1967-68 study were taken along an east-west survey route while the 1963-64 Lake Erie study incorporated nearshore as well as mid-lake samples in north-south traverses of the lake.

Table 12

WATER CHEMISTRY COMPARISONS 1963-64 - 1967-68
(Cleveland Program Office Data)
a)

		Western Basin			%	Central Basin			%	Eastern Basin			%	Total
		max.	min.	avg.	Change	max.	min.	avg.	Change	max.	min.	avg.	Change	Lake Avg.
Conductivity	1963-64	364	196	272		353	260	300		328	284	301		298.9
	1967-68	370	238	285	+4.8	330	283	312	+3.7	333	310	318	+5.6	312.6
Dissolved Solids	1963-64	220	110	162		239	137	178		233	150	179		177.6
	1967-68	247	135	170	+4.9	283	147	196	+10.1	297	138	204	+14.0	197.3
Total Solids	1963-64	250	140	181		218	159	185		240	167	188		185.8
	1967-68	356	147	188	+3.9	307	153	202	+9.2	308	175	220	+17.0	207.1
Chlorides	1963-64	34	10	21		46	19	24		31	21	24		23.9
	1967-68	26	10	19	-9.5	29	19	23	-4.2	28	24	25	+4.2	23.4
Silica	1963-64	5.0	0.3	1.20		9.6	0.2	0.68		3.5	0.2	0.47		0.64
	1967-68	1.87	0.43	1.06	-11.7	0.98	0.15	0.37	-45.6	0.72	0.18	0.37	-21.2	0.40
Soluble Phosphorus	1963-64	0.33	0.00	0.03		0.07	0.00	0.01		0.04	0.00	0.01		0.011
	1967-68	0.10	0.01	0.04	+33.3*	0.03	0.00	0.02	+100.0*	0.02	0.01	0.01	0.0	0.018
Total Phosphorus	1963-64	--	--	--		--	--	--		--	--	--		
	1967-68	0.19	0.02	0.06		0.05	0.01	0.02		0.08	0.01	0.02		0.022
Total Nitrogen	1963-64	2.66	0.17	0.71		1.30	0.07	0.43		1.18	0.10	0.42		0.44
	1967-68	1.98	0.27	0.74	+4.2	0.95	0.28	0.47	+9.3	0.75	0.30	0.47	+11.9	0.48
Organic Nitrogen	1963-64			0.36				0.25				0.24		0.25
	1967-68	0.71	0.07	0.37	+2.3	0.78	0.12	0.32	+28.0*	0.55	0.21	0.34	+41.6*	0.33

Table 12 (Cont'd)

WATER CHEMISTRY COMPARISONS 1963-64 - 1967-68

(Cleveland Program Office Data)

b)

		Western Basin			%	Central Basin			%	Eastern Basin			%	Total
		max.	min.	avg.	Change	max.	min.	avg.	Change	max.	min.	avg.	Change	Lake Avg.
Ammonia Nitrogen	1963-64	0.77	0.01	0.16		0.39	0.00	0.09		0.32	0.00	0.09		0.09
	1967-68	0.56	0.04	0.17	+6.3	0.21	0.02	0.10	9.0	0.17	0.04	0.07	-22.2	0.09
Nitrate Nitrogen	1963-64	1.50	0.02	0.12		0.84	0.00	0.09		0.85	0.01	0.09		0.09
	1967-68	0.96	0.01	0.20	66.7*	0.43	0.00	0.05	-44.4	0.16	0.00	0.06	-33.3	0.06
Chemical Oxygen Demand	1963-64	29.0	1.1	10.4		16.0	3.1	7.1		27.0	4.7	7.4		7.36
	1967-68	18.9	5.5	9.8	-5.8	11.9	5.2	8.6	+21.1*	11.0	6.1	8.2	+10.8	8.53
5-Day Biochemical Oxygen Demand	1963-64	--	--	--		--	--	--		--	--	--		
	1967-68	4.1	0.4	1.7		2.7	0.0	1.0		2.5	0.2	1.2		1.10
Alkalinity	1963-64	240	57	99		130	71	97		134	59	99		
	1967-68	105	75	90	-9.9	102	92	96	-1.0	109	92	98	-1.0	96.3
Eh	1963-64	--	--	--		--	--	--		--	--	--		
	1967-68	560	474	511		612	354	470		444	324	385		445
pH	1963-64													
	1967-68	8.8	7.6	8.3		8.9	7.7	8.4		8.7	7.5	8.3		8.36

* Eliminated from average to insure statistical validity.

SOURCE: Proceedings, Pollution of Lake Erie and Its Tributaries, F.W.P.C.A., Dept. Interior, Cleveland, Ohio, 1968.

Table 13

COMPARISON OF DETERMINATIONS MADE DURING DREDGING WITH NATIONAL WATER QUALITY STANDARDS AT ASHTABULA, OHIO

PARAMETER		USE & STANDARD	DISPOSAL AREA-LAKE		RIVER-HARBOR	
			Low	High	Low	High
ph	all uses:	5.0-9.0 any time (6.5-8.5 preferable)	8.06	8.13	6.83	7.31
DISSOLVED OXYGEN (mg/l)	industrial:	2.0 min. daily average 1.0 min. any time				
	aquatic life:	5.0 min. for 16 out of 24 hrs. 3.0 min. any time	10.99	11.23	11.18	11.64
DISSOLVED SOLIDS (mg/l)	industrial:	750 max. monthly average 1000 max. any time	212	223	173	253
TEMPERATURE	industrial:	95°F max. any time	NOT		APPLICABLE	
	aquatic life:	93°F max. May through December 78°F max. December through April				
TOXIC SUBSTANCES	aquatic life:	not to exceed 1/10 of the 48-hour median tolerance except when justified and approved	NO DATA		AT PRESENT	

SOURCE: Dredging and Water Quality Problems in the Great Lakes, Vol. 4, U. S. Army Corp Engineers, (1968) One STORET station, operated by the USGS at Jack's Automarine (0.80 mile point, station #04212700) has the most complete data available for the river over the longest period of time. Continuous monitoring of temperature, pH, conductivity and dissolved oxygen is performed at that station. It appears that the station is serviced approximately every two weeks. At that time water samples are taken because additional information appears sporadically in STORET for alkalinity, bicarbonate, nitrate, hardness, chloride, sulfate, fluoride, arsenic, mercury. Occasionally, other parameters are run such as copper, lead, nickel, silver, strontium, zinc, selium are entered into the system.

Table 14 lists recent available STORET data for the 1971-72-73 period which are most useful for comparison to present day values. Except for early data (1963-64), this is the most complete data set available in the system for the Ashtabula River. STORET station #502760 contains data for radioactivity parameters and several chlorinated hydrocarbons and pesticides. All parameters measured at this station yielded no trace amounts of the parameters tested with the exception of beta emissions (measured as 5.5 picocuries per liter). Parameters tested included the following:

Aldrin
Lindane
Heptachlor
Heptachlor Epoxide
DDD
DDE
DDT
Dieldrin
Endrin
Methoxychlor
Malathion
Parathion
M-Parathion

A recent STORET print-out (Aug. 24, 1973) yielded summary data for several years arranged in a much more convenient format than obtained July 16, 1973. STORET stations of interest in the Task II portion of this study are listed in Table 15.

Table 14

REPRESENTATIVE DATA FROM STORET STATION 04212700 (≃ 0.8 MILE POINT),
FOR 1971-73 (VALUES mg/l UNLESS OTHERWISE NOTED).

Date	T(°C)	Cond μ mho	DO	pH	T AIK	HCO_3	NO_3	TOC	Hard.	Cl^-	SO_4	F^-
71/11/01	18.3	1200	3.6	7.2	94	114	1.40	--	240	290	80	0.2
71/12/01	2.0	339	--	--	25	31	2.1	--	98	42	60	0.1
72/01/10	2.0	646	--	--	44	54	0.5	--	160	130	76	0.2
72/02/08	1.0	309	13.2	--	33	40	0.80	--	45	42	51	0.2
72/03/01	2.0	479	--	--	52	63	1.0	--	140	77	62	0.1
72/04/06	7.5	524	--	--	41	50	--	--	130	89	69	0.1
72/06/07	18.0	--	--	--	--	--	--	26.0	--	--	--	--
72/07/08	20.0	580	--	--	54	66	--	--	170	110	49	0.4
72/09/06	23.0	737	--	--	89	108	--	--	180	140	50	0.5
72/10/26	10.0	--	--	--	--	--	--	1.0	--	--	--	--
73/01/04	2.0	303	--	--	34	42	2.8	--	93	48	47	0.1
73/02/02	3.0	664	--	--	43	53	2.9	--	180	130	69	--
73/03/02	1.5	572	--	--	70	85	3.0	--	150	99	64	0.3

Table 15

APPLICABLE STORET STATIONS RELATED TO THIS STUDY
(F.B.-FIELDS BROOK, A.R.-ASHTABULA RIVER)

STORET #	MILEPOINT	LAT-LONG	DESCRIPTION
390024	6.3	41 51 20.0 080 45 44.0	USGS Gaging Station
380142	3.3	41 52 23.0 080 46 55.0	0.1 mi No of Rt 20
380141	2.3	41 52 30.0 080 47 42.0	E 24th St. Bridge
390027	A.R.1.5 FB-0.30	41 53 36.0 080 47 35.0	F. B. - E. 15th St.
0421270	0.80	41 54 00.0 080 47 44.0	Jack's Automarine
380137	0.70	41 54 07.0 080 47 55.0	5th St. Bridge
380136	0.00	41 54 38.0 080 47 55.0	A. R. Mouth
393303	Lake	41 54 30.0 080 48 38	Lake Erie 23' deep
--	Lake	41 54 38.0 080 47 54	Sludge Station 27' deep
--	Lake	41 56 20.0 080 46 04.0	Dredge Dump Station

Recent Ashtabula River-Fields Brook Data

Data obtained by the Cleveland Office of the USEPA and stored in their files in raw form were examined. The samples were collected between the period April 19 and May 5, 1973 and the values for each parameter averaged. Tables 16 (a) and (b) are a complete compilation of the available data. These data were entered into the STORET system in July 1974 (Zar, 1974; personal communication).

Table 16-a

RECENT CHEMICAL DATA FOR ASHTABULA RIVER (A.R.) AND FIELDS BROOK (F.B.)
MILEPOINTS ARE GIVEN IN PARENTHESIS. VALUES IN mg/l UNLESS OTHERWISE SPECIFIED.
SAMPLE DATES APRIL 19 - MAY 5, 1971, VALUES AVERAGED (DATA FROM CLEVELAND OFFICE EPA).

STORET STATION	TS	SS	Turb JTU	pH	COD	Cl^-	SO_4	Oil & Grease	Phenol μg/l	Cyanide
380142(2.3)	199	10	4	7.6	16.3	31	51	0.9	0.7	0.0
AR 1.57	431	14	8	7.8	24.6	129	72	1.1	5.0	0.0
421270(0.76)	465	27	15	7.7	21.1	138	75	1.0	2.0	0.0
390027 (FB0.38)	1100	58	25	8.0	26.8	405	137	1.7	10.0	0.0

Table 16-b

RECENT CHEMICAL DATA FOR ASHTABULA RIVER (A.R.) AND FIELDS BROOK (F.B.)
MILEPOINTS ARE GIVEN IN PARENTHESIS. VALUES IN mg/l UNLESS OTHERWISE SPECIFIED.
SAMPLE DATES APRIL 19 - MAY 5, 1971, VALUES AVERAGED (DATA FROM CLEVELAND OFFICE EPA).

STORET STATION	Ba μg/l	Sr μg/l	Cr μg/l	Cd μg/l	Pb μg/l	Cu μg/l	Fe μg/l	Zn μg/l	Ni μg/l	Ti μg/l	Hg μg/l	As μg/l
380142(2.3)	<333	<1400	<20	<40	<200	<42	950	<40	<60	<60	<0.1	<6.0
AR 1.57	<400	<1400	<30	<31	<200	<45	922	<49	<77	<60	<0.1	<6.3
421270(0.76)	<465	<1400	<23	<20	<200	<42	1100	<43	<69	<154	<0.1	<6.0
390027(FB0.38)	867	<1400	<296	<20	<200	<52	3164	<46	<86	<2704	<0.1	<6.0

Section 6
CURRENT WATER QUALITY AND BIOTA

This part of the study addressed the current water quality and biota present in the Ashtabula area. This program was begun as part of the Great Lakes Initiative Program and primarily addressed the current water quality picture of the Fields Brook-Ashtabula River and Harbor area. The sampling took place during three periods in 1973 and 1974. The delineation of current water quality over the reaches of Fields Brook was not a part of this effort with the exception of a sampling station located approximately one-half mile from its mouth and sampling for conductivity, chlorine residual and other parameters at the Fields Brook confluence with the Ashtabula River.

As previously discussed, nine major industrial discharges presently dispose of their effluent into Fields Brook and thence to the Ashtabula River although there are minor contributions to the river also from storm drainage and at least one small tributary in the study area near the Penn-Central bridge.

The United States-Canada Water Quality Agreement of 1972, the 1972 Amendments to the Federal Water Pollution Control Act (PL92-500), the special needs of the USEPA for allocation of waste loadings in this area, as well as a need to make projections of water quality based upon current data were the primary factors which led to the sampling study of the Ashtabula River and Harbor area.

The objectives of this water quality assessment program were to produce a comprehensive picture of the water borne impurities, standards violations, impact of major discharges and the aquatic biology in the Ashtabula River and Harbor area. Emphasis was placed upon the water quality which existed during a period of low river flow, although a limited special purpose sampling was performed during the spring also. Due to limitations of the scope of this study, major emphasis was placed upon the water quality rather than biota aspects.

Sampling Program

Field sampling for this project took place during three periods: 5 July 1973 (preliminary sampling at four stations; 4-11 September 1973 (primary sampling period); and 8-10 May 1974 (limited sampling for total residual chlorine, temperature, conductivity, Hg, Cr, Cu, Fe, and Na). These periods gave ample opportunities to sample, begin on-site analysis, and identify, for later investigation, potential problem areas.

During the September 1973 sampling period, Calspan's large mobile laboratory was located at Sutherland's Marina on the Ashtabula River near the 5th Street Bridge. This location enabled ready access to the harbor as well as the river and the mouth of Fields Brook by boat, and to return samples for immediate analysis. Many measurements were performed *in situ*. Samples were transported back to our mobile laboratory for further testing, refrigeration and transportation back to Calspan's water quality laboratory in refrigerated containers for further detailed analysis.

The purpose of the preliminary sampling of July 5, 1973 was to obtain information on the concentrations of parameters which might be expected and to assist in design of a sampling plan which would delineate problem areas. The sampling period from 8-10 May 1974, was a special, limited sampling which focused on specific objectives: (1) obtaining additional information on mercury, conductivity, and total residual chlorine at specific sites; and (2) to obtain samples for subsequent analysis for sodium, iron, chromium and copper.

Seven permanent sampling stations were selected for the purpose of this study with an eighth station added for completion during the first sampling series. Their locations were as follows (also Figure 3):

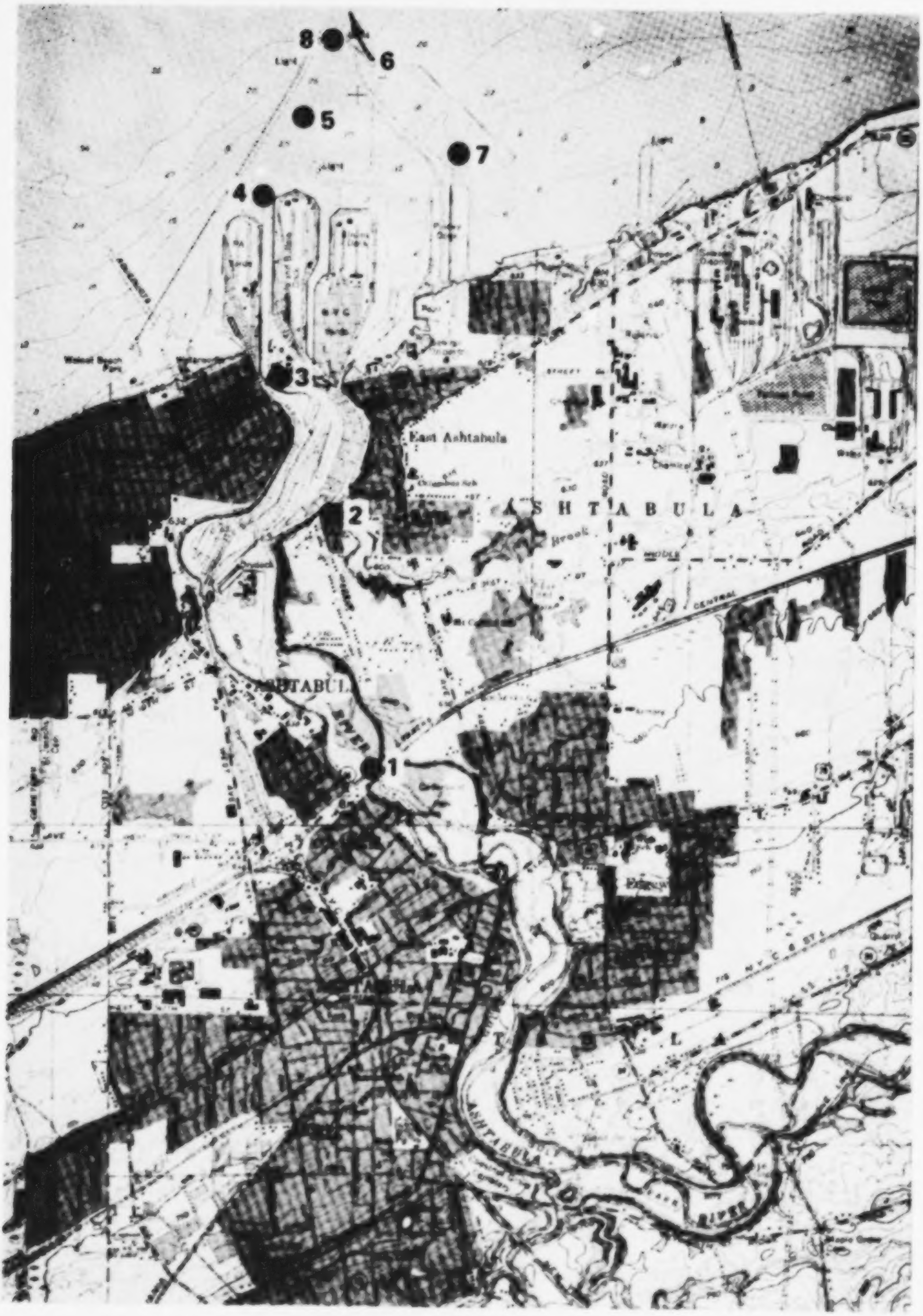

8
6
5
7
4
3
East Ashtabula
2
ASHTABULA
Brook
ASHTABULA
RIVER
1
ASHTABULA
RIVER

Figure 3 ASHTABULA AND FIELDS BROOK SAMPLE LOCATIONS

Station	Location
1	Above the 24th St. Bridge -- Ashtabula River
2	Fields Brook -- 15th St. Bridge
3	Ashtabula River -- 5th St. Bridge
4	Ashtabula River Mouth
5	Mid Harbor
6	1/4 mile outside breakwater light on Lake Erie
7	1/8 mile N. of Pinney Dock (Harbor)
8	Harbor Entrance

Each sampling station was carefully chosen so that an as-complete-as-possible water quality picture could be developed with a minimum number of sampling sites.

The primary sampling of 4-11 September 1973 was conducted during a period of excellent weather and low river flow (Table 17). Days were sunny to partly cloudy, temperatures in the 70-80°F range, and precipitation was zero except for the morning of 6 September (0.1 inch rain recorded). Conductivity, pH, DO, and temperature were measured in situ, after which samples were removed, refrigerated, and then shipped to Buffalo for immediate analysis of the parameters listed in the Task II Field Plan. Specially collected samples were obtained of the biota (phytoplankton, zooplankton and benthos), organic chemical constituents of Fields Brook water, and a sample of Fields Brook sediment near its mouth. Total residual chlorine was measured colorimetrically using the orthotolidine method.

As part of the development of a field plan, a sampling program was designed using the sample locations listed above. The types of analyses performed were broken into three separate groups. The following listing summarizes which analysis groups were performed in situ or on samples collected at each sample site (also Table 18).

Table 17

ASHTABULA RIVER FLOW CONDITIONS DURING PRIMARY FIELD SAMPLING PERIOD*

(4-11 September 1973)

Period (September)	Flow (c.f.s.)
4	0.7
5	0.6
6	4.0 (.1" rain)
7	3.5
8	2.8
9	1.8
10	1.3
11	1.1

*Source: USGS Water Resources Division, Columbus, Ohio.

Table 18
SAMPLE GROUPINGS

Group	Parameter
I	Dissolved Oxygen
	Total Dissolved Solids
	Total Organic Carbon
	Chloride
	Chlorine(Total Residual)
	pH
II	Coliform (total)
	Coliform (fecal)
	Settleable Solids
	Suspended Solids
	Oil and Grease (extractibles with Trichlorotrifluoroethane)
III	PCB's
	Pesticides (Chlorinated hydrocarbons)
	Selected.Organics (GC Analysis)

	Metals (12)
Hardness	
Alkalinity	As
BOD_5, BOD_{20}	Ba
COD	Cd
Kjeldahl Nitrogen	Cr
Nitrate	Cu
Chloride	Fe
Phenols	Hg
Ammonia	Pb
Cyanide	Ni
Phosphorus (total)	Se
Fluoride	Ti
	Zn

Station	Group
1	I*, II
2	I*, II, III
3	I*, II
4	I*, II
5	I*, II, III
6	I*, II, III
7	I*, II

Group I parameters were run at all stations and at three depths (1 meter depth, intermediate depth, 1 meter above the bottom). Group II parameters were run on at least one sample depth (1 meter depth). Group III parameters were run at surface (1 meter depth) only. In addition, dissolved oxygen, conductivity and temperature data were obtained at 1 and 2 foot intervals at most stations. Table 18 lists the parameters analyzed for each Group.

Methods employed for the water quality analysis follow the procedures outlined in Appendix 1 and which are presented in "Methods of Chemical Analysis of Water and Wastes" (EPA, 1971) and "Standard Methods for the Examination of Water and Wastewater", 13th edition, 1971.

The Ashtabula River is classified as a warm water fishery by the State of Ohio. Standards applicable to the river have been revised recently (1973) and proposed 1974 revisions subjected to public hearings during August 1974. Revisions were to be finalized and issued for public notice in December 1974 during which time the final draft of this report was prepared. Appendix 2 lists the most relevant general water quality standards applicable to the Ashtabula River.

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*All depths for T, DO, Conductivity; three depths for TDS, Cl^-, Cl_2, pH.

Results

As part of a reconnaissance investigation to determine final choices of stations and ranges of water quality parameters which might be present in the study area, a preliminary sampling was performed on 5 July 1974. The results of analysis for twenty-eight parameters are presented in Table 19 as the AS I series. Evaluation of this data indicated that some of the most important water quality parameters for the examination of the study area were total dissolved solids, chlorides, and conductivity. Since this was a limited purpose sampling, water sampling equipment was not employed other than glass gallon containers, and no in situ measurements were made, although the strong chlorine odor associated with Fields Brook was noted. The particularly high values of dissolved solids noted at the Fields Brook mouth and downstream showed the influence of the discharges even though river flow was higher than the subsequent sampling in September. Based upon this sampling series, subsequent sample station locations and choice of parameters were made.

The AS II sampling series was a sampling series for biota, and data on the biota is presented later in this section.

The primary sampling period resulted in a series of detailed sampling and analysis at stations selected according to the sampling program previously discussed. In addition to specialty analyses (such as metals, organics, etc. which are described later), twenty-eight water quality parameters were obtained at each station. Tables 20, 21, and 22 list the results of the analyses for three dates during the September 1973 sampling period. The AS III series has an additional sampling station (8) located at the harbor entrance. Examination of the data on the three sampling dates indicates that the significant water quality parameters in the study area are conductivity, dissolved solids, nitrates, total residual chlorine, and chlorides. It is clear that the source of most anomalous concentrations of parameters is Fields Brook, and this indicates the importance of the brook's contribution to water quality during low flow conditions. The flow of Fields Brook nearly accounts for the discharge of the Ashtabula during these periods. Concentrations of the above parameters in the Fields Brook samples (upstream of any possible lake effect or water back-up) indicate the source of most significant water quality parameters.

Table 19

ASHTABULA RIVER AS-I

PARAMETER		1 (UPSTREAM (GAGING STA.))	2 (FIELDS BK. MOUTH)	3 (5th ST.)	4 (HARBOR)
DATE 5 JULY 1973					
HARDNESS (as ppm $CaCO_3$)		115	325	200	137
pH		7.10	8.50	8.35	8.85
ALKALINITY (as ppm $CaCO_3$)		73.8	88.4	86.8	92.6
TOC mg/	mg/ℓ	10	24	9	10
SUSPENDED SOLIDS	mg/ℓ	22	27	39	19
DISSOLVED SOLIDS	mg/ℓ	214	1514	658	272
TOTAL SOLIDS	mg/ℓ	236	1541	697	291
CHLORIDES	mg/ℓ	15	280	220	35
OIL & GREASE	mg/ℓ	< 1.0	3.6	< 1.0	< 1.0
NITRATE NITROGEN (as N)	mg/ℓ	< 0.10	1.80	1.50	0.90
KJELDAHL NITROGEN (as N)	mg/ℓ	< 0.50	0.75	0.75	0.56
SULFATE	mg/ℓ	60	72	63	45
TOTAL PHOSPHORUS (as P)	mg/ℓ	< 0.1	< 0.1	< 0.1	< 0.1
SURFACTANTS	mg/ℓ	< 0.05	< 0.05	< 0.05	< 0.05
PHENOLS	mg/ℓ	0.030	0.050	0.010	0.030
CALCIUM	mg/ℓ	24	93	48	29
MAGNESIUM	mg/ℓ	7.5	7.2	7.4	7.0
COBALT	mg/ℓ	< 0.03	< 0.03	< 0.03	< 0.03
IRON	mg/ℓ	0.120	0.270	0.310	0.160
CHROMIUM	mg/ℓ	< 0.02	< 0.02	< 0.02	< 0.02
CADMIUM	mg/ℓ	< 0.005	< 0.005	< 0.005	< 0.005
MANGANESE	mg/ℓ	0.025	0.050	0.100	0.025
LEAD	mg/ℓ	< 0.02	< 0.02	< 0.02	< 0.02
NICKEL	mg/ℓ	< 0.02	< 0.02	< 0.02	< 0.02
COPPER	mg/ℓ	0.025	0.030	0.020	0.030
ZINC	mg/ℓ	0.014	0.010	0.020	0.014
SODIUM	mg/ℓ	12	750	78	15
MERCURY	mg/ℓ	< 0.001	< 0.001	< 0.001	< 0.001

Table 20

ASHTABULA RIVER AS-III

PARAMETER		1	2	3	4	5	6	7	8
DATE 5 SEPT 73									
pH		7.60	7.35	7.08	7.35	8.70	8.30	8.60	7.90
TEMPERATURE	°C	24.5	31.0	27.0	25.1	25.9	25.0	25.0	25.8
HARDNESS (as mg/ℓ $CaCO_3$)		214	415	234	159	131	130	132	133
ALKALINITY (as mg/ℓ $CaCO_3$)		98.5	108	91.5	93.5	94.5	92.5	94.0	93.0
CONDUCTIVITY	μ mho's/cm	600	2650	1400	590	329	295	335	315
DISSOLVED OXYGEN	mg/ℓ	7.7	7.5	4.3	6.0	8.6	8.4	8.2	8.1
BOD (5 days)	mg/ℓ	1.05	9.90	2.20	1.60	1.10	0.95	0.83	0.90
BOD (20 days)	mg/ℓ	–	11.0	–	–	–	1.33	–	1.84
COD	mg/ℓ	12.9	4.3	8.6	8.6	4.3	25.8	12.9	–
TOC	mg/ℓ	33	30	29	28	29	23	25	24
SOLIDS (SETTLEABLE)	mℓ/ℓ	< 0.1	0.2	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
SOLIDS (SUSPENDED)	mg/ℓ	35	50	32	30	18	15	15	20
SOLIDS (DISSOLVED)	mg/ℓ	372	1612	887	387	201	206	210	231
SOLIDS (TOTAL)	mg/ℓ	407	1662	919	417	219	221	225	251
COLIFORM (TOTAL)	#/100 mℓ	1600	< 2	> 6000	1200	720	10	80	6
COLIFORM (FECAL)	#/100 mℓ	180	< 2	300	150	80	< 2	10	< 2
PHOSPHORUS (TOTAL)	mg/ℓP	0.85	1.08	1.25	0.74	0.60	0.94	0.85	1.40
PHOSPHORUS (ORTHO)	mg/ℓP	< 0.02	0.07	< 0.02	< 0.02	< 0.02	0.02	< 0.02	< 0.02
AMMONIA	mg/ℓ	0.175	0.50	0.13	< 0.10	< 0.10	< 0.10	0.10	< 0.10
KJELDAHL NITROGEN	mg/ℓ	0.23	0.43	0.65	0.23	0.42	0.23	0.33	0.23
NITRATE	mg/ℓ	0.07	6.0	1.20	1.60	0.05	< 0.02	0.06	0.07
PHENOLS	mg/ℓ	< 0.01	0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
CYANIDE	mg/ℓ	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005
CHLORIDE	mg/ℓ	52	570	285	101	33	35	33	35
FLUORIDE	mg/ℓ	0.20	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05
SULFATE	mg/ℓ	120	140	88	43	29	28	27	31
CHLORINE (TOTAL)	mg/ℓ	< 0.010	12.0	0.050	0.040	0.010	< 0.005	0.010	0.005
OILS AND GREASE	mg/ℓ	4.5	2.0	2.0	2.0	1.5	2.5	2.0	< 1.0

Table 21

ASHTABULA RIVER AS-IV

PARAMETER	1	2	3	4	5	6	7
DATE 8 SEPT 73							
pH	8.70	6.55	7.30	8.60	8.10	8.70	8.65
TEMPERATURE °C	19.0	27.0	24.9	24.0	24.5	24.8	24.9
HARDNESS (as mg/ℓ $CaCO_3$)	192	420	198	138	137	130	128
ALKALINITY (as mg/ℓ $CaCO_3$)	95.5	86.5	93.0	92.5	93.5	92.0	92.0
CONDUCTIVITY µ mho's/cm	445	2200	880	332	310	280	290
DISSOLVED OXYGEN mg/ℓ	7.3	6.5	5.7	6.9	6.7	7.2	7.1
BOD (5 days) mg/ℓ	0.30	8.60	0.70	0.80	1.50	1.30	1.40
BOD (20 days) mg/ℓ	2.05	9.35	1.20	2.50	2.35	2.70	1.80
COD mg/ℓ	16.3	30.2	18.5	18.5	4.7	4.70	14.0
TOC mg/ℓ	24	21	21	18	20	19	18
SOLIDS (SETTLEABLE) mℓ/ℓ	< 0.1	0.2	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
SOLIDS (SUSPENDED) mg/ℓ	8	37	22	15	13	< 5	< 5
SOLIDS (DISSOLVED) mg/ℓ	360	1504	534	238	209	216	178
SOLIDS (TOTAL) mg/ℓ	368	1541	556	253	222	216	178
COLIFORM (TOTAL) #/100 mℓ	7000	< 2	5600	110	20	6	< 2
COLIFORM (FECAL) #/100 mℓ	4000	< 2	1000	40	< 10	< 2	< 2
PHOSPHORUS (TOTAL) mg/ℓP	0.48	0.40	0.14	0.24	0.28	0.32	0.63
PHOSPHORUS (ORTHO) mg/ℓP	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02
AMMONIA mg/ℓ	0.20	0.10	0.20	< 0.05	< 0.05	< 0.05	0.30
KJELDAHL NITROGEN mg/ℓ	0.46	0.75	0.75	0.46	0.28	0.19	0.28
NITRATE mg/ℓ	0.07	4.40	4.70	0.10	0.08	0.05	0.05
PHENOLS mg/ℓ	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010
CYANIDE mg/ℓ	–	–	–	–	–	–	–
CHLORIDE mg/ℓ	44	554	174	44	38	26	29
FLUORIDE mg/ℓ	0.20	0.20	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05
SULFATE mg/ℓ	116	100	68	30	29	28	29
CHLORINE (TOTAL) mg/ℓ	< 0.005	1.10	0.01	< 0.01	0.01	0.01	0.05
OILS AND GREASE mg/ℓ	3.5	3.5	2.0	3.0	1.0	< 1.0	1.5

Table 22

ASHTABULA RIVER AS-V

PARAMETER	1	2	3	4	5	6	7
DATE 10 SEPT 73							
pH	8.80	8.65	8.10	8.75	8.75	8.90	7.85
TEMPERATURE °C	17.9	24.0	23.3	23.2	23.2	23.7	23.5
HARDNESS (as mg/ℓ $CaCO_3$)	201	439	200	132	133	129	131
ALKALINITY (as mg/ℓ $CaCO_3$)	94.0	91.0	93.0	92.0	93.5	94.0	93.0
CONDUCTIVITY μ mho's/cm	420	2210	825	318	308	288	300
DISSOLVED OXYGEN mg/ℓ	8.5	6.6	8.0	7.8	7.8	8.2	7.7
BOD (5 days) mg/ℓ	1.90	2.55	3.30	1.75	2.30	1.90	2.20
BOD (20 days) mg/ℓ	2.30	3.00	4.90	2.10	2.40	2.00	2.20
COD mg/ℓ	22.2	6.6	13.4	8.9	15.6	11.1	15.6
TOC mg/ℓ	21	20	18	19	17	17	18
SOLIDS (SETTLEABLE) mℓ/ℓ	< 0.1	0.15	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
SOLIDS (SUSPENDED) mg/ℓ	6.5	28	21	8	7	1	5
SOLIDS (DISSOLVED) mg/ℓ	302	1495	503	205	443	180	184
SOLIDS (TOTAL) mg/ℓ	309	1523	524	213	450	181	189
COLIFORM (TOTAL) #/100 mℓ	400	< 2	6600	320	300	< 2	10
COLIFORM (FECAL) #/100 mℓ	55	< 2	1400	30	40	< 2	2
PHOSPHORUS (TOTAL) mg/ℓP	0.12	0.06	0.16	0.14	< 0.02	0.04	< 0.02
PHOSPHORUS (ORTHO) mg/ℓP	< 0.02	0.03	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02
AMMONIA mg/ℓ	0.05	< 0.05	< 0.05	0.05	< 0.05	< 0.05	0.05
KJELDAHL NITROGEN mg/ℓ	0.28	0.36	0.56	1.49	0.42	0.47	0.42
NITRATE mg/ℓ	< 0.02	5.0	2.0	0.06	0.06	0.04	< 0.02
PHENOLS mg/ℓ	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010
CYANIDE mg/ℓ	–	–	–	–	–	–	–
CHLORIDE mg/ℓ	41	598	166	35	36	26	29
FLUORIDE mg/ℓ	0.20	0.20	0.10	< 0.05	< 0.05	< 0.05	< 0.05
SULFATE mg/ℓ	115	110	55	33	29	30	29
CHLORINE (TOTAL) mg/ℓ	0.02	6.5	0.02	0.01	0.01	< 0.01	0.01
OILS AND GREASE mg/ℓ	2.0	2.0	3.5	< 1.0	1.5	< 1.0	1.5

Organic Chemical Constituents. According to the Field Plan prepared for this program, a single water sample from Fields Brook was to be analyzed for its organic chemical constituents. The results reported here, however, include analysis of samples from Fields Brook (2), Mid-harbor (5), and the Offshore (6) sampling stations. The method used for extraction was similar to extractive procedure for pesticides (EPA, 1971). One liter samples were extracted three times with a hexane-diethyl ether (85-15) mixture. The hexane-ether extracts were then concentrated to a volume of five milliliters using a Kuderna Danish evaporator. Aliquots of this sample with no additional clean-up were injected directly into a gas chromatograph. A gas chromatograph (Hewlett-Packard 5700) with an electron capture detector was used. This detector was selected since most of the materials to be surveyed were chlorinated species and excellent detection limits would be obtained. The separation column was a 6' x 1/4" OD glass, packed with 1.5% OV17 and 1.95% QF-1 on Gas Chrom Q, 80-100 mesh.

Most of the components eluted very early in the chromatogram. A major component was detected in all three of the samples. The component could not be identified in view of the limited program restrictions, however, the relative response of this component in each sample is listed below:

Fields Brook (2)	290,000
Mid-Harbor (5)	9,300
Outside (6)	1,200

Some idea of the boiling point of the material can be postulated since the unknown material elutes after hexachloroethane and before hexachlorobenzene. It may be assumed that the material is halogenated due to the detection of the component in lake water. Due to the sensitivity of our detector for halogenated compounds, it still could be detected even though it was present in extremely dilute concentrations. A non-halogenated compound probably would not have been detected. The source of the material is clearly Fields Brook.

Other components were also detected in the samples, but none of the components could be identified as being those listed in the table below. Some of the eluted components observed could be lower chlorinated ethanes and/or ethylenes that elute near the tail of the solvent peak.

Materials Surveyed

(Results from gas chromatographic scans of extract concentrates)

- Tetrachloroethane
- Hexachloroethane
- Monochlorobenzene
- 1,2,4 Trichlorohenzene
- Hexachlorobenzene
- Toluene Diisocyanate
- Dimethyl phthalate
- Dibutyl phthalate

None of these components were detected as present in the samples.

In addition to the above, a survey was made for the presence of seventeen chlorinated pesticides and PCB's to determine if they were present or absent in samples from Fields Brook (2), mid-harbor (5), and offshore (6). Table 23 lists the results of the analyses. None of the listed parameters was found to be present above the limits of detectability (<.01 μg/l for chlorinated pesticides and < .1 μg/l for PCB's).

Metals. Analyses for heavy metals concentrations were performed for all sampling stations for the following metals: As, Ba, Cd, Cr, Cu, Fe, Hg, Ni, Pb, Se, Ti, Zn. Tables 24, 25 a,b list the results of the analyses. Most parameters are present in the μg/l range with the exception of barium and titanium. The analysis for titanium proved to be difficult, and it was not possible to refine our measurement below 1 mg/l . Specific values worth highlighting here include the presence of mercury concentrations averaging 1.3-1.4 μg/l in Fields Brook at Station 2. Nickel concentrations in Fields Brook on 5 September were slightly higher than other sample locations and this was true also on 8 September. Nickel concentrations on 10 September were the same at all locations. Iron concentrations at Fields Brook and the upstream station were higher than the lake and harbor areas probably reflecting the

Table 23

ASHTABULA RIVER AS-III

CHLORINATED PESTICIDES AND POLYCHLORINATED BIPHENYLS

PARAMETER		2	5	6
DATE 5 SEPT 73				
α-BHC	µg/ℓ	< 0.01	< 0.01	< 0.01
LINDANE	µg/ℓ	< 0.01	< 0.01	< 0.01
HEPTACHLOR	µg/ℓ	< 0.01	< 0.01	< 0.01
ALDRIN	µg/ℓ	< 0.01	< 0.01	< 0.01
KELTHANE	µg/ℓ	< 0.01	< 0.01	< 0.01
HEPTACHLOR EPOXIDE	µg/ℓ	< 0.01	< 0.01	< 0.01
γ-CHLORDANE	µg/ℓ	< 0.01	< 0.01	< 0.01
ENDOSULFAN I	µg/ℓ	< 0.01	< 0.01	< 0.01
p,p'-DDE	µg/ℓ	< 0.01	< 0.01	< 0.01
DIELDRIN	µg/ℓ	< 0.01	< 0.01	< 0.01
ENDRIN	µg/ℓ	< 0.01	< 0.01	< 0.01
o,p'-DDT	µg/ℓ	< 0.01	< 0.01	< 0.01
ENDOSULFAN II	µg/ℓ	< 0.01	< 0.01	< 0.01
p,p'-DDD	µg/ℓ	< 0.01	< 0.01	< 0.01
p,p'-DDT	µg/ℓ	< 0.01	< 0.01	< 0.01
METHOXYCHLOR	µg/ℓ	< 0.01	< 0.01	< 0.01
PCB's	µg/ℓ	< 0.1	< 0.1	< 0.1

Table 24

METALS

ASTABULA RIVER AS-III

PARAMETER		1	2	3	4	5	6	7	8
DATE 5 SEPT 73									
ARSENIC	μg/ℓ	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10
BARIUM	mg/ℓ	1.4	2.9	2.1	1.1	1.5	1.1	1.0	1.1
CADMIUM	μg/ℓ	1.0	2.5	1.0	0.3	0.3	0.3	0.3	0.3
CHROMIUM	μg/ℓ	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5
COPPER	μg/ℓ	6	10	8	9	7	7	8	8
IRON	μg/ℓ	260	250	60	60	80	30	120	40
MERCURY	μg/ℓ	0.6	1.4	0.6	0.6	1.2	4.8	0.9	1.4
NICKEL	μg/ℓ	5	15	< 5	< 5	< 5	< 5	< 5	< 5
LEAD	μg/ℓ	5	5	5	3	< 3	< 3	< 3	5
SELENIUM	μg/ℓ	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5
TITANIUM	mg/ℓ	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0
ZINC	μg/ℓ	16	13	17	15	12	22	12	22

Table 25

METALS

(a) ASHTABULA RIVER AS-IV

PARAMETER		1	2	3	4	5	6	7
DATE 8 SEPT 73								
ARSENIC	μg/ℓ	< 10	< 10	< 10	< 10	< 10	< 10	< 10
BARIUM	mg/ℓ	1.5	2.5	2.0	1.5	1.5	1.0	1.0
CADMIUM	μg/ℓ	1.0	1.0	0.6	0.6	< 0.3	< 0.3	< 0.3
CHROMIUM	μg/ℓ	< 5	< 5	< 5	< 5	< 5	< 5	< 5
COPPER	μg/ℓ	6	10	8	8	8	8	8
IRON	μg/ℓ	360	140	260	240	280	20	70
MERCURY	μg/ℓ	< 0.3	1.3	< 0.3	< 0.3	< 0.3	< 0.5	< 0.5
NICKEL	μg/ℓ	< 5	5	< 5	< 5	< 5	< 5	< 5
LEAD	μg/ℓ	4	< 3	4	4	< 3	< 3	< 3
SELENIUM	μg/ℓ	< 5	< 5	< 5	< 5	< 5	< 5	< 5
TITANIUM	mg/ℓ	< 1	< 1	< 1	< 1	< 1	< 1	< 1
ZINC	μg/ℓ	12	22	10	10	8	22	16

(b) ASHTABULA RIVER AS-V

PARAMETER		1	2	3	4	5	6	7
DATE 10 SEPT 73								
ARSENIC	μg/ℓ	< 10	< 10	< 10	< 10	< 10	< 10	< 10
BARIUM	mg/ℓ	< 1.0	3.5	2.0	1.0	1.5	1.0	1.0
CADMIUM	μg/ℓ	< 0.3	0.5	0.5	0.5	< 0.3	< 0.3	< 0.3
CHROMIUM	μg/ℓ	< 5	< 5	< 5	< 5	< 5	< 5	< 5
COPPER	μg/ℓ	10	10	9	8	9	8	8
IRON	μg/ℓ	360	110	180	80	90	30	60
MERCURY	μg/ℓ	4.3	1.3	< 0.3	0.4	< 0.3	< 0.3	< 0.3
NICKEL	μg/ℓ	< 5	< 5	< 5	< 5	< 5	< 5	< 5
LEAD	μg/ℓ	< 3	< 3	< 3	< 3	< 3	< 3	< 3
SELENIUM	μg/ℓ	< 5	< 5	< 5	< 5	< 5	< 5	< 5
TITANIUM	mg/ℓ	< 1	< 1	< 1	< 1	< 1	< 1	< 1
ZINC	μg/ℓ	6	10	9	7	5	5	7

leaching of iron from soils and its presence as a component of process water in plant effluents.

Mercury, due to recent interest in its toxicity, has been examined in greater detail in this report because of seemingly anomalous concentrations upstream at Station 1 on 10 September 1973 (4.3 μg/l) and offshore at Station 6 on 5 September (4.8 μg/l). In addition to Calspan's sampling, the Ohio District office has conducted sampling and mercury analysis on three separate occasions during 1973.

As discussed above, sampling of the Ashtabula River and Harbor, nearshore Lake Erie and Fields Brook, was performed during the period 4-11 September 1973. During this period, anomalous concentrations of mercury were discovered at selected stations, and the information has been assembled here together with subsequent data in an attempt to identify the possible source. The results compiled, therefore, represent Calspan's efforts on 4-11 September 1973, USEPA sampling on April 11, June 25, and July 31, 1973, and Calspan sampling on 8-10 May 1974.

Previously it had been thought that Fields Brook industries supply a relatively constant source of mercury, but the presence of concentrations of mercury of up to three times greater than samples obtained from Fields Brook suggests either another source (especially if dilution is taken into consideration), or the possibility that sporadic, high concentrations are discharged from time to time and are not mixed well with river water. The latter could be favored because of the high temperatures measured in Fields Brook compared to river water producing a layering effect with little mixing with cooler, denser waters below and thus less dilution than expected.

Data compiled on mercury from the above sources is presented in Table 26. Several important points are worth noting here concerning the data gathered by the USEPA and Calspan. Further sampling of upstream sources including a small tributary near the Penn Central Bridge and of the river water upstream of the first small falls and at the USGS gazing station indicates

Table 26

MERCURY DATA (ug/ℓ)[1]

STATION	4/11/73	6/25	7/31	9/5	9/8	9/10	12/10	5/8/74	5/8	5/9	5/9	5/10
UPSTREAM – PC BRIDGE	–	–	–	0.6	< 0.3	4.3	–	< 0.5	< 0.5	< 0.5	< 0.5	–
ASHTABULA RIVER – E. 24th ST.	0.4*	0.3*	0.2*	–	–	–	2.2(*,4)	0.4	< 0.5	< 0.5	< 0.5	–
FIELDS BROOK – STATE RD.(2)	–	–	–	–	–	–	–	–	–	–	–	21
FIELDS BROOK – STATE RD.(3)	–	–	–	–	–	–	–	–	–	–	–	1.9
FIELDS BROOK – RT. 20	0.2*	0.8*	0.3*	–	–	–	–	–	–	–	–	–
FIELDS BROOK – E. 15th ST.	0.8*	0.5*	0.4*	1.4	1.3	1.3	–	1.4	2.0	4.2	2.9	5.8
FIELDS BROOK MOUTH	–	–	–	–	–	–	–	1.5	2.0	4.6	3.7	–
ASHTABULA RIVER – E. 6th ST.	0.2*	0.6*	0.2*	0.6	< 0.3	< 0.3	–	0.8	< 0.5	< 0.7	< 0.5	–
ASHTABULA RIVER (MILEPOINT 0.0)	–	–	–	0.6	< 0.3	0.4	–	–	–	–	–	–
ASHTABULA MID HARBOR	–	–	–	1.2	< 0.3	< 0.3	–	–	–	–	–	–
HARBOR ENTRANCE	–	–	–	1.4	–	–	–	–	–	–	–	–
OFFSHORE	–	–	–	4.8	< 0.5	< 0.3	–	–	–	–	–	–
PINNEY DOCK	–	–	–	0.9	< 0.5	< 0.3	–	–	–	–	–	–

* USEPA DATA (PERSONAL COMMUNICATION WINKLHOFER TO ZAR, JAN. 28, 1974)

(1) – OHIO WATER QUALITY STANDARD FOR MERCURY 12/18/73 0.5 ug/ℓ

(2) – EAST SIDE OF STATE RD. BRIDGE OVER FIELDS BROOK (UPSTREAM)

(3) – WEST SIDE OF STATE RD. BRIDGE OVER FIELDS BROOK (OUTFALL SAMPLE)

(4) – SAMPLE FROM OUTFALL ON E. 24th ST. KNOWN TO THE USEPA TO CONTAIN DISCHARGES FROM ASHTABULA GENERAL HOSPITAL AND A SANITARY BYPASS.

values of <0.5 µg/l Hg on all sampling occasions during May 8 and 9, 1974. This appears to rule out upstream or tributary sources of mercury, above the Penn Central Bridge (our Station 1). USEPA sampling in Fields Brook and the Ashtabula River were performed during a period of flow of 160 cfs (4/11), 13.3 cfs (6/25), and 2.75 cfs (7/31). Considerable dilution might be expected during the early sampling period but with such an interval separating the dates, it is doubtful if the subsequent samplings which were taken in such a limited area might reveal (other than by chance) anomalous concentrations of mercury. The intensive sampling both in frequency and locations conducted as part of the September and May sampling serves as a baseline for examination of the mercury problem, at least in a preliminary way. The USEPA supplementary sampling at an outfall located at E 24st St (which was described as containing discharges from the Ashtabula General Hospital and a sanitary bypass) was found to contain 2.2 µg/l mercury on 12/10/73. This points out a need to monitor this discharge and determine the mercury concentration, flow, and duration of discharges. Certain disinfecting agents are known to contain mercury, although they are not so commonly used today as in the past.

Examination of Table 26 indicates that over the dates sampled Fields Brook concentrations of mercury are quite variable and in one instance (5/10/74) quite high (21 µg/l) compared to the Ohio standard for mercury (0.5 µg/l). The concentration of mercury upstream of the State Rd bridge points to a source as does the value for the outfall in the west side of the bridge (1.9 µg/l). The area to the east is a lowland, swampy area with normally sluggish flow. Therefore, high runoff caused by precipitation may directly influence the mercury concentration in Fields Brook. The influence of Fields Brook may be even more important when examination of the data for 9/5/73 is made. A concentration increasing from the river mouth to the offshore station indicated the probability that movement of mercury in solution over the upper layers of water took place probably during the last 24 hours, perhaps less. Sampling in Fields Brook and in the river on 8 September indicated no anomalous values but two days later a high concentration of mercury (4.3 µg/l) was found at the Penn-Central Bridge. Apparent upstream movement of water (lake effect) extends to this station and the wind was blowing generally onshore that day. It is, therefore, postulated that a high concentration of mercury was discharged within the previous 24 hours and the warm, Fields Brook waters were pushed, relatively undiluted upstream. Confirmation of this effect and of the levels and source(s) of mercury by detailed field measurement is believed necessary and is recommended by this report. The most effective manner to perform this study will be by on-site analysis and a detailed sampling program.

Conductivity and Dissolved Solids. Extensive and detailed in situ measurement of conductivity was made as part of this effort and partially reported previously in Tables 20-22. In addition, conductivity data as a function of depth will be reported later in this section as part of the data obtained during the September 5 sampling. As part of the field sampling portion of this work, a conductivity profile was made by use of a technique of towing the probe at a known depth (1 meter) and velocity. A profile of the results of this data collection is presented in Figure 4. Comparison of the data gathered using this technique with measurements made on station indicates complete agreement and has proven the method to be a rapid, accurate method of assessing the dissolved solids content of the water. Dissolved solids concentrations in Fields Brook ranging from 1495 to 1612 mg/l were measured during the period of the conductivity investigation. Dissolved solids concentrations and, in particular, chloride concentrations vary in the same order downstream from the Fields Brook mouth and also in the upstream direction. Conductivity is a rapid, relatively inexpensive measurements of dissolved solids, and it is recommended for use in areas such as Ashtabula where wide variations of dissolved solids can be expected. The profile illustrates graphically what the tabular data also shows; that Fields Brook is the primary source of dissolved solids in the lower Ashtabula River. Measurement of the dissolved solids and conductivity in Ashtabula Harbor and offshore, however, indicates little variation from what can be considered to be ambient, although in general harbor values are higher than offshore values.

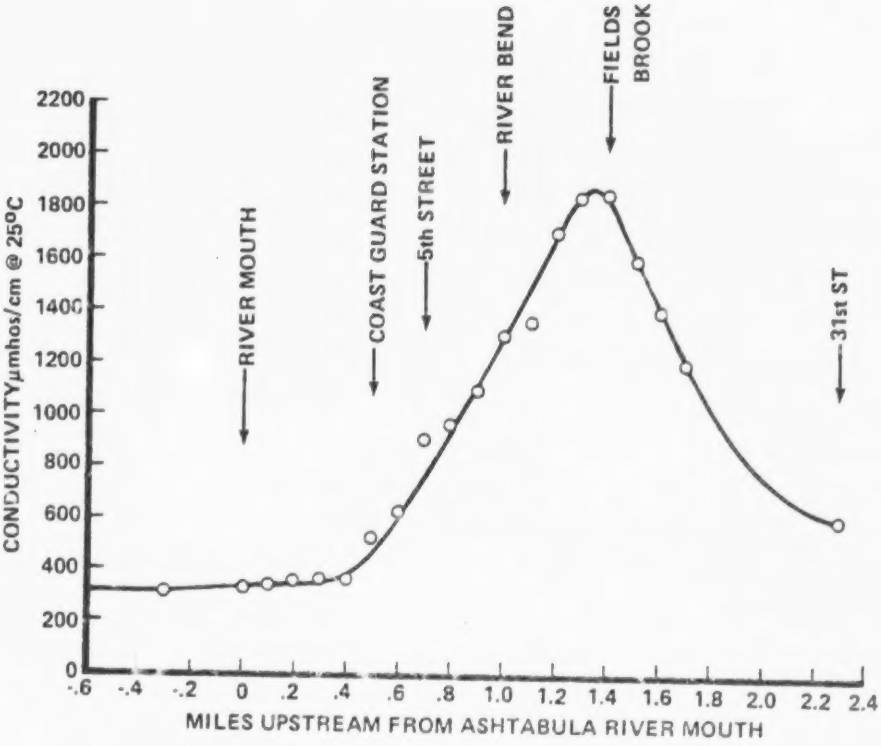

Figure 4 CONDUCTIVITY PROFILE OF ASHTABULA RIVER

Chlorine Residuals

Industries located in the Fields Brook area are known to discharge concentrations of chlorine (present in the form of calcium hypochlorite) in concentration levels which frequently vary from 40 to 120 mg/l . These levels, as will be discussed later, represent an extremely toxic condition to biota in Fields Brook and in the vicinity of its mouth. Brungs (1973) recommended certain "safe" levels of chlorine residual which are far exceeded in most of the lower Ashtabula as measured in this study. Data have become available recently on the levels of toxicity of chlorine to several fish species, phytoplankton and zooplankton (Brungs, 1973; Brook and Baker, 1972; Hamilton, et al., 1970). In general, recommended disinfection levels are between 0.5 and 1.0 mg/l which is well below known toxicity levels to mammals; however, concentrations not to exceed 0.002 mg/l (continuously) have been recommended for the protection of most aquatic organisms. Accurate determination of residual chlorine (free and combined) is best obtained by use of the amperometric method (see Standard Methods, 1971). The orthotolidine method with pre-mixed visual standards was used in the field during this study. As part of Calspan's investigation of determining what levels of chlorine might be expected in the Ashtabula River and Fields Brook, a theoretical study of the prediction of chlorine residuals in a flowing stream was undertaken (Pereira, Terlecky, and Yaksich, 1974). A copy of the report of that investigation is included here as Appendix 3. The fundamental assumptions are to determine what the safe levels are for biota in the river and then calculate by use of a model what levels can be tolerated at the discharge point(s). Based upon an examination of the data requirements (chlorine demand, free and residual chlorine measurements all along the course of the brook, other parameters), it was determined that the costs associated with obtaining the data and testing the model were too large for the current effort. Therefore, after detailed examination of a method of approach, and determination of a method of testing the model, no further work on the model was done. It was hoped that with the detailed chlorine data obtained here, a projection of chlorine concentrations could be made in an empirical way.

Tables on water quality presented in a previous section list data obtained on total chlorine residual. In addition to that data, additional measurements were made at selected points on September 5-6, 1973 and are presented in Figure 5. Measurements of total chlorine residual were also made on 8-10 May 1974 for selected stations and are presented in Table 27. High concentrations of chlorine residual can be observed in Fields Brook. The outfall sampled at the west side of the bridge at State Road on Fields Brook had a value of 35.0 mg/l total residual chlorine when sampled on May 10, 1974. Depending upon conditions of flow, time, etc., values measured in the Ashtabula River at the mouth of Fields Brook are clearly quite high. Values measured within an hour or two on each sampling day illustrate the dilution effect of the river with values of 0.03 and 0.05 mg/l recorded. The detection limit for the orthotolidine method as used in this study was 0.01 mg/l.

Table 27 Total Chlorine Residual (mg/l) 8-10 May 1974

Station (#)	5/8	5/8	5/9	5/9	5/10
Upstream (1)	< 0.010	< 0.010	< 0.010	< 0.010	-
Fields Brook - 15th St (2)	6.5	4.5	4.5	3.0	2.4
Fields Brook - State Rd (W)	-	-	-	-	0.2
Fields Brook - State Rd (Outfall)	-	-	-	-	35.0
Mouth of Fields Brook	9.5	4.0	3.0	3.0	-
Ashtabula River (3)	0.03	0.05	0.05	0.05	-

Sodium. Although measurement of sodium concentrations was not a part of this effort originally, it was decided to obtain analyses for sodium for possible use in flushing time calculations such as performed previously by the Army Corps of Engineers as presented in Section 2. As a result, 75 samples were analyzed for sodium and the results are presented here as Table 28. It was determined that the prime source of sodium was Fields Brook with sporadic additional contributions from upstream sources. Highway runoff may be the source of this upstream sodium which was originally derived from deicing salt (V, 1-3).

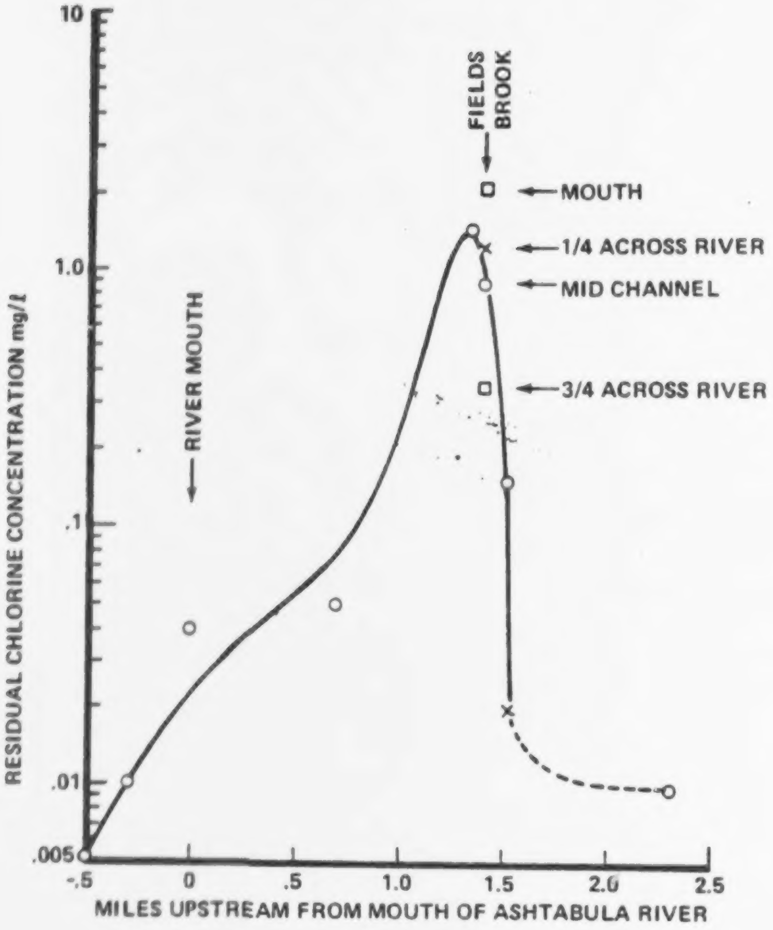

Figure 5 TOTAL RESIDUAL CHLORINE DISTRIBUTION SEPT. 5-6, 1973

Table 28 Sodium Content of Ashtabula Water Samples

(Concentrations in mg/l; ppm)

Sample No., Station	AS III	AS IV	AS V
1-1	41	32	37
2-1	340	310	350
3-1	210	100	88
3-2	86	95	86
3-3	64	78	170
4-1	60	24.0	21.0
4-2	20.0	23.5	22.5
4-3	16.5	23.0	27.0
5-1	21.0	20.5	21.0
5-2	37.0	22.0	21.0
5-3	18.5	24.0	19.5
6-1	15.0	14.0	15.5
6-2	15.0	14.0	16.0
6-3	14.0	14.5	19.5
7-1	20.0	16.0	16.0
7-2	23.5	16.0	15.0
7-3	20.5	16.5	15.0
8-1	21.0	-	-
8-2	16.0	-	-
8-3	15.5	-	-

Additional Samples Analyzed and the Sodium Concentrations:

	Na (mg/l)
Fields Brook at the River	330
III 6-5	16.5
III 6-9	14.5
III 3-7	23.5
III 3-11	220
III 5-7	19.0
III 6-7	15.5
III 2-3	340
III 3-9	115
III 5-9	19.5
III 5-5	20.5
III 1-3	42
IV 1-2	32
III 1-1a	35
V 1-3	500

Sediment Chemistry. A brief examination of the sediment chemistry of Fields Brook was made in an effort to determine what contributions are made by the brook to the sediments of the river. A single sample was obtained from near the mouth of Fields Brook and analyses for several metals were performed. The results are presented in Table 29. Significant contributions of barium, chromium, copper, iron, nickel, lead, and zinc were found. Mercury concentration in the sediment was 2.6 μg per gram of sediment dry weight.

Variation of Water Quality with Depth

Data obtained for eight parameters at surface (1 meter), intermediate depth, and one meter above the bottom was assembled for each of the sample stations examined in this study. The upstream and Fields Brook samples were taken at an intermediate depth because of the shallowness of the water at each site. Temperature, pH, conductivity, dissolved oxygen, total dissolved solids, total organic carbon, total residual chlorine, and chloride concentration were measured on September 5. Table 30 lists the results of the analysis. Changes in concentrations of most parameters with depth were not pronounced with the exception of temperature, conductivity, dissolved solids and chloride concentrations at the 5th St. Bridge. Dissolved oxygen concentrations are expected to be reduced near the bottom especially if the organic nature of these sediments is considered. Chlorine concentrations at Fields Brook (12.0 mg/l), 5th St. Bridge and the mouth of the river were higher than expected.

Table 29
FIELDS BROOK SEDIMENT

PARAMETER	FIELDS BROOK SEDIMENT
DATE 6 SEPT 73	
μg/g DRY WEIGHT	
ARSENIC	< 1.0
BARIUM	860
CADMIUM	17
CHROMIUM	158
COPPER	80
IRON	33,000
MERCURY	2.6
NICKEL	59
LEAD	61
SELENIUM	< 2
TITANIUM	– *
ZINC	210

*TOO MUCH FLAME EMISSION TO GIVE AN ACCURATE ANALYSIS.

Table 30

ASHTABULA RIVER AS-III

SAMPLE	DEPTH (meters)	TEMP °C	pH	COND (µmho/cm)	DO (mg/ℓ)	DISSOLVED SOLIDS (mg/ℓ)	TOC (mg/ℓ)	CHLORINE RESIDUAL (mg/ℓ)	CHLORIDE (mg/ℓ)
DATE 5 SEPT 73									
UPSTREAM (1)	0.2	24.5	7.6	600	7.7	372	33	< 0.010	52
FIELDS BROOK-15th STREET (2)	0.5	31.0	7.35	2650	7.5	1612	30	12.0	570
5th STREET BRIDGE (3)	1.0	27.0	7.08	1400	4.3	887	29	0.050	285
	3.4	26.1	7.48	1000	3.9	479	26	0.100	148
	5.5	25.2	7.40	700	3.3	441	29	< 0.010	124
MOUTH OF RIVER (4)	1.0	25.1	7.35	590	6.0	387	28	0.040	101
	4.6	24.2	7.85	320	5.9	230	26	0.020	35
	8.2	24.0	8.05	310	6.4	221	26	0.020	29
MID HARBOR (5)	1.0	25.9	8.70	329	8.6	201	29	0.010	35
	4.9	24.9	8.45	430	7.1	287	25	0.025	64
	8.8	23.5	8.60	310	5.4	202	27	0.010	27
OUTSIDE HARBOR (6)	1.0	25.0	8.30	295	8.4	206	23	< 0.005	35
	6.7	24.5	7.75	300	7.8	217	25	< 0.006	29
	12.8	17.0	7.55	275	2.0	216	34	0.100	26
OFF PINNEY DOCK (7)	1.0	25.0	8.60	335	8.2	210	25	0.010	33
	4.9	24.9	8.35	350	7.6	243	25	0.010	36
	9.2	24.0	7.60	338	4.9	225	27	0.040	34
HARBOR ENTRANCE (8)	1.0	25.8	7.90	315	8.1	231	24	0.005	35
	5.5	24.9	8.30	302	7.5	201	25	< 0.005	29
	10.0	23.8	8.25	302	5.0	212	29	0.020	27

Biota Sampling and Analysis

Locations were chosen (Stations 1, 2, 3, 5, 6) for plankton sampling (surface, intermediate, near bottom) and sediment sampling for benthic invertebrates (sludge worms). A great deal of literature has evolved in recent years relating organisms to water quality, and therefore, as a minimum, these groups should be characterized in any study of water quality. Limited benthic sampling was performed in this study.

Phytoplankton were identified from collections made in the following manner: A three liter sample from the desired depth was collected and poured through a plankton net. The sample of plankton thus obtained was to be transfered to a small sample container and 70% alcohol fixative solution was used for preservation. An additional one liter sample of water from each depth was collected, preserved and also transfered to the laboratory for analysis of the phytoplankton. A double sample technique was preferred because of the concern that fine sized forms (diatoms) might escape the plankton net used. Water was collected in specific amounts because of a need for absolute knowledge of the volume sampled. We have been dissatisfied with techniques of towing in the past and feel that with this method, the sample volume which has passed through the net can be determined precisely.

An Eckman dredge was used for the bottom biota sampling of sludge contents. _Limnodrilus_ sp. appeared to be the dominant form in the study area. The sample was dredged up, a known volume of sediment was placed on a specially designed sieve and the worms were sieved out and preserved for later identification. The Eckman dredge used had a sampling area of 36 in^2. Results of benthos collections at each station were obtained by at least two casts, and the analyzed samples reflect the combined results. The presence or absence of other benthic invertebrates such as _Musculium transversum_ and _Pisidium_ sp. (molluscs) was noted, and specimens collected if present. Sediment samples were removed and transported for later analysis, if necessary.

Biota

Samples were obtained from Stations 1, 2, 3, 5 and 6 during the period 4-11 September 1973. The "as is" sample was digested and centrifuged with a goal of looking at the diatom population at each site only, while the filtered sample was taken to assess the population characteristics of the entire plankton population. It should be noted that the nets used were #12 mesh. Organisms less than 100 µ could pass through this net. In general, the results of the study indicate that communities can be identified which are common to the lower Ashtabula River, the Harbor, and the Lake. *In situ* chemical measurements made during sampling are presented in Table 31.

Samples from Station 1 (upstream, a lotic environment) contained little diversity of plankton in comparison to the lower river and harbor (Table 32). A maximum of 12 inches of water during the sampling period (except for pools) was observed, and black bass (*Micropterus*), suckers (unidentified), and crayfish (unidentified) were also observed. No fish samples were captured for later identification. No benthic organisms were obtained from the gravel and rock river bottom at this time. The dominant diatom was *Cyclotella* at this station. This observation *per se* does not provide definitive information because, within this genus, species found occupy a great diversity of environments ranging from oligotrophic to eutrophic.

Station 2, Fields Brook, also a shallow environment, yielded high residual chlorine values (see Table 31). Vegetation at the brook's edge was damaged. Plankton samples contained low organism counts. Three *Pediastrum* species were present, as well as *Keratella*, a rotifier. (Table 32) Diatoms were present in significant amounts. No benthic organisms were recovered from the sediments.

In the Ashtabula River, at the 5th St. Bridge (approximately one mile below the mouth of Fields Brook), plankton samples were obtained at 1 meter, 3.6 meters, and 6.7 meters. Organisms recovered were common to Lake Erie. Benthic samples from Station 3 revealed a rich population of small tubificid Oligochaeta (115/36 in^2; 5000/m^2). The plankton are listed in Tables 32, 33, and 34.

Table 31 DESCRIPTION OF VARIOUS WATER QUALITY PARAMETERS AT STATION LOCATION AT THE TIME OF BIOTA SAMPLING

	Station 1	Station 2	Station 3	Station 3	Station 3	Station 6	Station 6	Station 6	Station 5	Station 5	Station 5
Date (Sept.73)	4	4	5	5	5	5	5	5	5	5	5
Depth of Sample (plankton)	surface	surface	1 meter	3.6 m	6.7 m	1m	6.7m	12.8m	1m	4.9m	8.8 m
Temperature of H_2O	29.5°C	31°C	27°C	26.1°C	25.2°C	25°C	24.5°C	17°C	25.9°C	24.9°C	23.5°C
Dissolved oxygen	7.8ppm	7.5ppm	4.3ppm	3.9ppm	3.3ppm	8.4ppm	7.8ppm	2.0ppm	8.6ppm	7.1ppm	5.4ppm
Chlorine residual	<0.1ppm	8.0ppm	0.05ppm	0.1ppm	0.01ppm	<0.005ppm	<0.005ppm	0.01ppm	0.01ppm	0.025ppm	0.01ppm
pH	7.3	7.35	7.08	7.48	7.40	8.30	7.75	7.55	8.7	8.45	8.6
Conductivity (umhos)	620	2650	1400	1000	700	295	300	275	329	430	310

Table 32 STATIONS FROM WHICH PLANKTONIC ORGANISMS WERE OBTAINED AND THE ABUNDANCE IN TERMS OF CELLS PER LITER - SURFACE SAMPLES.

Station 1 (6 in. depth) Upper Ashtabula River		Station 2 (6 in. depth) Fields Brook		Station 3 (1 m) Ashtabula River		Station 6 (1 m) Lake Erie		Station 5 (1 m) Harbor	
Cyclotella	68	Pediastrum simplex	12	Closteriopsis longissima	83	Staurastrum sp.	183	Keratella cochlearis	92
Cymbella	4	Pediastrum sp.^{1}	6	Ceratium hirundinella	33	Ceratium hirundinella	67	Fragilaria sp.	75
Cladoceran (damaged)	1	Pediastrum sp.^{2}	6	Keratella cochlearis	25	Keratella cochlearis	67	Ceratium hirundinella	67
Pediastrum sp. simplex	2	Keratella cochlearis	12	Staurastrum sp.	8	Fragilaria sp.	50	Staurastrum sp.	50
		Navicula	*	Fragilaria sp.	8	Closteriopsis longissima	25	Anacystis	50
		Cyclotella	*			Pediastrum simplex	17	Pediastrum simplex	33
								Tabellaria	25
								Closteriopsis longissima	25
								Stephanodiscus	25
								Difflugia	25
								Cosmarium	8
								Botryococcus	8

* will be quantitatively reported in specific diatom studies

Table 33 STATIONS FROM WHICH PLANKTONIC ORGANISMS WERE OBTAINED AND THE ABUNDANCE OF PLANKTON PRESENT IN TERMS OF CELLS PER LITER MID-DEPTH

Station No. 3 (3.6 meters) Ashtabula River		Station 6 (6.7 meters) Lake Erie		Station 5 (4.9 meters) Harbor	
Pediastrum simplex	250	*Ceratium hirundinella*	100	*Closteriopsis longissima*	317
Keratella cochlearis	100	*Keratella cochlearis*	58	*Fragilaria* sp.	200
Ceratium hirundinella	75	*Anacystis* sp.	58	*Pediastrum simplex*	167
Codonella cratera	17	*Closteriopsis longissima*	58	*Ceratium hirundinella*	150
Copepods (damaged)	17	*Staurastrum* sp.	33	*Keratella cochlearis*	83
Various diatoms	--	*Diaptomus* sp.	25	*Anacystis* sp.	75
Staurastrum sp.	17	*Fragilaria* sp.	25	*Staurastrum* sp.	50
				Difflugia sp.	25

Table 34 STATIONS FROM WHICH PLANKTONIC ORGANISMS WERE OBTAINED AND THE ABUNDANCE OF PLANKTON PRESENT IN TERMS OF CELLS PER LITER - BOTTOM DEPTH

Station No. 3 (6.7 meters) Ashtabula River		Station No. 6 (12.8 meters) Lake Erie		Station No. 5 (8.8 meters) Harbor	
Ceratium hirundinella	100	Staurastrum sp.	92	Fragilaria sp.	75
Pediastrum simplex	75	Closteriopsis longissima	92	Pediastrum simplex	75
Staurastrum sp.	58	Pediastrum simplex	83	Ceratium hirundinella	58
Fragilaria sp.	58	Ceratium hirundinella	33	Closteriopsis longissima	50
Closteriopsis longissima	42	Fragilaria sp.	25	Staurastrum sp.	42
Keratella cochlearis	25	Keratella cochlearis	17	Anacystis	33
Diaptomus sp.	17	Anacystis sp	17	Keratella cochlearis	8
Tabellaria sp.	17	Codonella cratera	8	Tabellaria sp.	8
Anacystis sp.	17	Asterionella sp.	8		
Difflugia sp.	8				
Cladoceran	8				

Plankton samples from the harbor (Station 5) were obtained at depths of 1 meter, 4.9 meters, and 8.8 meters (Tables 32, 33, 34). The harbor water contained a more numerous and diverse plankton community than the lake or river (Table 33). Benthic organisms from mid-harbor sediments contained approximately 50 "unhealthy"* tubificids, one leech, 5 Pisidium (clam) and 2 tiny Sphaerids (Sphaerium) per 36 sq in. This was similar to the 1950 collection of benthic organisms (Brown, State of Ohio, 1953).

Plankton samples from Station 6 (Lake Erie) were obtained at 1 meter, 6.7 meters, and 12.8 meters. The dominant plankters at this station were no more diverse than that found at Station 3, but some species were more abundant (Tables 32, 33, 34). Most of the organisms common in the lake were also present in the river at Station 3. Lake sediments contained few tubificids (3/36 sq in) and tiny Sphaerium (clam).

Cell counts observed in these measurements are lower than might normally be expected in the Great Lakes. However, several reasons may be cited for these low counts:

(1) The use of a #12 mesh allows organisms finer than 100 μ to escape the net and thus be inadequately represented.

(2) The presence of potentially toxic conditions in harbors like Ashtabula with low natural flow during the time of sampling and relatively high discharges of industrial waste. A comparison of this habor with open lake conditions is thus difficult to make.

(3) Forms such as Closteriopsis longissima (a large form caught on the net) are present in low numbers also.

(4) Diatom cell numbers were also low at Station 6, the most open water station in the study. Another study, Ohio EPA (1973), also observed low cell counts.

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*Tubificids examined were present in very poor condition for identification at Station 5 (sluggish, flaccid) in contrast to those recovered from Stations 3 and 6 (active, solid).

(5) The "as is" samples did not indicate large number of organisms which would refute the above observation of low cell numbers.

Diatom Analysis

Diatom communities have been summarized on samples obtained from the upper Ashtabula River (Station 1, above Penn Central RR Bridge), Fields Brook (Station 2), the Ashtabula River below the entrance of Fields Brook (5th St. Bridge, Station 3), mid-harbor (Station 5), and outside the harbor (Station 6).

Diatoms were concentrated from 300 ml of sample by gentle filtration through a 0.45 μ membrane filter. The filter, debris, and organic materials were digested by concentrated sulfuric acid at room temperature for 23 hours. The resulting diatom sediment was washed in distilled water until the pH of the solution was approximately 7. Microscope slides were made using Caedax and were examined at 430X and 1000X (with oil) magnification.

The abundance of each diatom genus or species was expressed as the percent of the total number of cells counted. In nearly all cases at least 100 individual diatoms were examined if 100 could be counted within 45 minutes. Tables 35-39 list the diatoms identified and their abundance at each locality.

In the upper Ashtabula River, the diatom, Cyclotella, dominated the plankton community (Table 35). This station, when compared to others of this study, was not significantly different in diversity, though Field's Brook and Lake Erie appeared to have the fewest number of genera. The primary organisms found in the water were diatoms.

Table 35 Diatom Distribution of the Upper Ashtabula River (Station 1)

DIATOM	ABUNDANCE (%)
Cyclotella sp	64.0
Navicula sp	13.2
Tetracyclus lacrustis *	4.6
Cymbella sp	3.2
Rhoicosphenia curvata	3.2
Synedra sp	1.9
Frustulia sp	1.9
Surirella sp	1.2
Nitzschia sp	1.2
Fragilaria crotonensis	1.2
Cocconeis sp	1.2
Melosira sp	0.6
Amphora sp	0.6
Gyrosigma sp	0.6
Hantzschia sp	0.6

* Identification is not consistent with the fact that T. lacrustis has not previously been reported in Ohio

Table 36 Diatom Distribution in Fields Brook (Station 2)

DIATOM	ABUNDANCE (%)
Fragilaria crotonensis	32.0
Stephanodiscus sp	17.8
Coscinodiscus sp	10.2
Tabellaria sp	9.3
Melosira sp	6.8
Nitzschia sp	5.9
Navicula sp	5.9
Surirella sp	4.2
Cyclotella sp	2.5
Fragilaria	2.5
Cocconeis sp	1.7
Rhoicosphenia curvata	1.7

Table 37 Diatom Distribution in the Ashtabula River (Station 3 - Mile Point 0.7, 5th St. Bridge)

DIATOM (1 Meter)	%	DIATOM (3.35 m)	%	DIATOM (6.70 m)	%
Cyclotella sp	54.5	Cyclotella sp	35.0	Cyclotella sp	22.3
Nitzschia sp	22.0	Navicula sp	23.0	Navicula sp	16.5
Navicula sp	11.0	Nitzschia sp	15.5	Nitzschia sp	14.0
Coscinodiscus sp	3.0	Cymbella sp	6.5	Cymbella sp	9.1
Synedra sp	2.5	Coscinodiscus sp	5.0	Fragilaria crotonensis	9.1
Cymbella sp	2.0	Melosira sp	3.0	Coscinodiscus sp	8.3
Cocconeis sp	1.5	Fragilaria sp	2.5	Melosira sp	3.3
Surirella sp	1.5	Caloneis sp	2.5	Surirella sp	3.3
Rhoicosphenia curvata		Tabellaria sp	2.0	Stephanodiscus sp	2.5
Melosira sp	1	Gomphonema sp	1.5	Amphora sp	1.7
Diatoma vulgare	1	Stephanodiscus sp	1.5	Cocconeis sp	1.7
Fragilaria sp		Surirella sp	1.0	Rhoicosphenia curvata	1.7
		Synedra sp	1.0	Diatoma vulgare	0.8
		Diatoma vulgare	0.5	Tetracyclus sp	0.8
		Tetracyclus sp	0.5	Tabellaria sp	0.8

Table 38 Diatom Abundance in Ashtabula Harbor (Mid-Harbor, Station 5)

DIATOM (1 meter)	%	DIATOM (4.88 m)	%	DIATOM (8.84 m)	%
Stephanodiscus sp	19.5	*Cyclotella* sp	23.3	*Fragilaria virescens*	18.2
Fragilaria crotonensis	16.9	*Fragilaria crotonensis*	20.0	*Cyclotella* sp	18.0
Cyclotella sp	14.5	*Stephanodiscus* sp	19.5	*Stephanodiscus* sp	12.0
Coscinodiscus sp	13.0	*Melosira* sp	7.3	*Melosira*	7.8
Fragilaria virescens	8.5	*Tabellaria fenestrata*	6.0	*Diatoma vulgare*	7.8
Nitzschia sp	8.0	*Navicula* sp	5.3	*Tabellaria fenestrata*	6.6
Tabellaria fenestrata	7.3	*Nitzschia* sp	4.6	*Nitzschia* sp	6.0
Melosira sp	3.6	*Coscinodiscus*	4.6	*Coscinodiscus* sp	6.0
Rhoicosphenia curvata	3.0	*Rhoicosphenia curvata*	2.6	*Fragilaria crotonensis*	4.6
Navicula sp	3.0	*Diatoma vulgare*	2.0	*Navicula* sp	3.6
Cocconeis sp	1.5	*Cocconeis* sp	2.0	*Rhoicosphenia curvata*	3.0
Surirella sp	1.5	*Gyrosigma* sp	1.3	*Achnanthes* sp	3.0
		Amphora sp	0.7	*Surirella* sp.	1.8
		Fragilaria virescens	0.7	*Cocconeis* sp	1.2
				Gyrosigma sp	0.6

Table 39 Diatom Abundance in Lake Erie off Ashtabula Harbor (Station 6). Diatoms encountered in surface sample were rare. Only ten individuals were encountered during a 45 minute counting period.

DIATOM (1 meter)	%	DIATOM (6.7 m)	%	DIATOM (12.8m)	%
Fragilaria sp	60	*Fragilaria crotonensis*	45.0	*Cyclotella* sp	15.0
Nitzschia sp	20	*Fragilaria virescens*	20.0	*Tabellaria fenestrata*	14.0
Navicula sp	10	*Tabellaria fenestrata*	15.0	*Melosira* sp	12.5
Stephanodiscus	10	*Stephanodiscus* sp	5.3	*Stephanodiscus* sp	12.5
		Nitzschia sp	5.3	*Fragilaria* sp	11.5
		Cyclotella sp	4.0	*Coscinodiscus* sp	9.2
		Navicula sp	2.5	*Nitzschia*	9.2
		Coscinodiscus sp	1.3	*Navicula* sp	5.8
		Melosira	1.3	*Diatoma vulgare*	4.6
		Cocconeis	1.3	*Gyrosigma* sp	2.3
				Surirella sp	1.2
				Cocconeis sp	1.2
				***	

*** In addition to the diatoms counted in this sample, a significant amount of fragments belonging to the Genera *Cymbella* and *Fragilaria* were observed as being present at this depth.

Fields Brook, containing 8 ppm residual chlorine, also yielded live green algae and rotifers, as well as many species of diatoms. In view of the high residual chlorine values, these organisms are thought to have been carried downstream to the sampling area from areas of Fields Brook above industrial discharges. Fragilaria crotonensis dominated the diatom community of Fields Brook. Table 36 lists the diatoms recovered from water samples. Stephanodiscus, Coscinodiscus, and Tabellaria were found in highest concentrations with Fragilaria. Only two significant diatom species (5%) were recovered in the upper Ashtabula River, but seven species of significance were recovered from Fields Brook and represented 88% of the total diatom community. It was not within the scope of this study to sample and assess attached (sessile) algal forms. Planktonic diatom forms were of major concern. A "control" sample of attached forms in the areas of sampling would have had to be obtained by a diver. In addition, back-up of lake waters to the Penn Central Bridge affected any samples which would have been gathered below the first small falls at Station 1. Station 1 biota samples were taken at a point just above the small falls in a shallow, lotic environment.

Greatest diversity and abundance of diatoms occurred at Station 3, the lower Ashtabula River. The influence of Field's Brook could be seen by the presence of Stephanodiscus and Coscinodiscus in significant concentrations. Cyclotella and Navicula dominated, as in the upper River. Table 37 summarizes the results of studies at three depths.

In the mid-harbor waters, the diatom community represented contributions from lake, river and Field's Brook communities (Table 38). Dominance was shared by Stephanodiscus (Field's Brook), Cyclotella (River), Fragilaria crotonensis (Field's Brook), Fragilaria virescens (Lake Erie) and Coscinodiscus (Field's Brook). These species represented 85-72.5 percent of the diatom community at Station 5. Melosira was recovered here in significant concentrations at 4.9 meters and 8.8 meters.

Surface water samples from Lake Erie, outside the harbor, were nearly devoid of diatoms. Concentrations increased with depth, but were low even in bottom samples (Table 39). Dominance varied more with depth than it did at other stations. *Fragilaria*, *Tabellaria*, *Stephanodiscus*, *Melosira* (6.7 meters) and *Cyclotella* (at 6.7 meters) were the dominant diatoms. In 1950 (State of Ohio, 1953) the lake water at Ashtabula was dominated by *Melosira*, *Stephanodiscus*, *Fragilaria* and *Asterionella*. In the present study, no *Asterionella* was recovered in any amount. *Melosira* was present but not dominant, except at 6.7 meters where it represented 12.5% of the diatom community. *Asterionella* has been the dominant organism in Lake Erie for many years but began to disappear from samples after 1950. It is known to peak in spring and winter, which may explain the absence of *Asterionella* from these late summer samples. Therefore, no significance should be attached to a seasonal form which might not have been sampled in the present study. *Fragilaria* occurred frequently in samples observed for the present study and often dominated. This diatom has dominated many samples from Lake Erie since 1950 and has a late summer or early autumn peak.

The low biomass, low diversity (in relation to studies of unaffected areas of Lake Erie), and dominance of only a few species at Station 6 may indicate toxic conditions at the harbor mouth. (See also discussion of low cell counts under *Biota*).

Many of the algae genera represented in samples from the Ashtabula River, Field's Brook, Harbor and Lake Erie have been classified as organic pollution tolerant organisms (Palmer, 1969). *Nitzschia* and *Navicula* appear high on the tolerance list. *Synedra*, *Melosira*, *Cyclotella*, *Pediastrum*, *Fragilaria*, *Surirella*, and *Stephanodiscus* appear on the first half of the pollution tolerant genera list.

As association was noted in samples in which *Fragilaria crotonensis* dominated. *Tabellaria fenestrata*, *Stephanodiscus* and *Coscinodiscus* were also found in high concentrations.

Species, such as Rhoicosphenia curvata, Navicula sp, Cymbella sp, and Synedra were recovered only in the River. These were also recovered in the Harbor, where River influence was felt.

Diversity and biomass of diatoms increased with depth at nearly all stations. This could be due to an increase of available nutrients with depth, photo inhibition of diatoms, and sinking of diatoms.

Section 7
DISCUSSION

Water Quality Aspects

An overall view of the data presented in Section 6 indicates that the prime water quality problems associated with the Fields Brook-Ashtabula River area involve discharges of chlorine, dissolved solids, chlorides, and mercury. Fecal coliform bacteria have been found present to a degree which indicates discharge of sanitary sewage at selected points in the river. The lift bridge at 5th Street is a case in point where fecal coliform values have revealed the presence of a sanitary discharge not connected to the municipal sewage treatment facility. Occasional upstream samples contain high concentrations of fecal coliform, but the sampling program here was not designed in such detail as to determine their location. For the periods sampled, the harbor or lake area sites did not contain values of coliform which were high. In view of the residual chlorine values present over much of the river and harbor areas, coliform values could be expected to be low. Over the next 2-3 years, however, lowering of residual chlorine in discharges will necessitate increased attention to this parameter.

The general water quality picture appears to have improved somewhat over the past several years in Ashtabula. Floating algal masses, high fecal coliform values, and noticeably pigmented discharges have all decreased during the period 1968-present. With the exception of near bottom values, dissolved oxygen concentrations at most stations are in the 6.5-8 mg/l range. BOD and COD values for Fields Brook usually (AS III, IV) are above those for the river in the near vicinity of Fields Brook. The AS V sampling series was a notable exception (the BOD on that date was lower than the previous sampling days). Settleable solids measurements, were, in general, negligible at all stations with the exception of Station 2, Fields Brook, measuring a relatively constant 0.15-0.2 mg/l. Suspended solids measurements were relatively low at all stations including the Pinney Dock area where new work dredging was being done.

With the exception of Fields Brook, nutrient elements present as total phosphorous at most stations yielded values which were relatively similar within each sampling series but varied greatly from date to date. Phosphates (ortho) remained at low levels for most of the stations on each date sampled. Nitrate levels at Fields Brook and Station 3 were elevated and remained at higher levels throughout the study. Nitrate levels measured at Fields Brook 4.4-6.0 mg/l for the three dates in the primary sampling series. Downstream values generally decreased with increasing distance from Fields Brook. Values of nutrient parameters measured in the harbor can be considered as conducive for the stimulation of phytoplankton and algal growth in the harbor. This does not take into account the presence of potentially toxic components. Phosphate contributions from Fields Brook to the river and harbor are relatively minor, but it does appear clear that the nitrate source is Fields Brook.

Sulfate concentrations are high upstream and decrease in the downstream direction. Fields Brook sulfate levels are close to upstream values. This decrease demonstrates the dilution of Fields Brook and upstream water by lake water.

Organic Constituents

The presence of a major unknown organic component in Fields Brook waters was detected in the limited sampling and analysis program for organic chemicals. The results of this preliminary survey indicate that the unknown material is halogenated and that it elutes after hexachloroethane and before hexachlorobenzene. None of the other materials surveyed by gas chromatography were above the limits of detectability for several organic components. A survey of chlorinated pesticides and PCB's indicated none to be present above the limits of detectability (Table 23).

Metals

Most metals surveyed in this study appear to be at sufficiently low levels at all stations as to present no major problems. With the exception of iron, metal ions present in Fields Brook are normally at levels higher than the other sampling sites. Mercury, however, demonstrates the complexity of circulation patterns in the river and harbor, and the need for closely controlled sampling patterns and frequency. The Ohio standard for mercury is 0.5 µg/l . This standard is exceeded in nearly every measurement made in Fields Brook during the course of this program and by previous USEPA sampling. Examination of Table 26 points out the need for closely spaced and frequent sampling. USEPA samplings were done during periods of higher flow than sampling done in the primary period of this study. A return visit to Ashtabula during May 1974 indicated the presence of mercury concentrations at Fields Brook (Station 2) and the Fields Brook mouth to be from 3 to nearly 12 times the maximum allowable concentrations. From time to time high concentrations of mercury are discharged and appear at other locations at fairly high levels (e.g., 4.8 µg/l , Station 6 on 9/5/73; 4.3 µg/l , Station 1 on 9/10/73). An elevated concentration of mercury was measured by the USEPA at an outfall at E. 24th St of 2.2 µg/l on 12/10/73. However, follow-up sampling by Calspan in May 1974 indicated no significant presence of mercury in the river at that location on four separate occasions. A measurement on Fields Brook made on 5/10/74 at the east side of the State Road Bridge yielded 21 µg/l mercury, while measurement of an outfall on the west side of the bridge yielded 1.9 µg/l . Both measurements are clearly in excess of the Ohio standard of 0.5 µg/l. It appears that the presence of mercury in these two samples is very real because a measurement at Station 2 downstream on Fields Brook on the same day indicated the presence of a concentration of 5.8 µg/l Hg. The fact that warm, less dense water was discharged from Fields Brook at all sampling times may account for the presence of high concentrations of mercury appearing at selected sampling locations during this study. Warm Fields Brook waters are postulated to override colder, more dense river and harbor waters and thus be prevented from full mixing and dilution. This is true even though high dissolved solids concentrations are discharged and contribute to density increases.

We recommend a detailed, comprehensive survey preferably with an on-site analysis capability (Atomic Absorption) be conducted during the late Spring, Summer and early Fall of the year to determine the levels and degree of compliance with water quality standards for discharges into Fields Brook. Further, we recommend that the outfall near the E. 24th St area be monitored in addition.

Chlorine Discharges

Brungs' (1973) recommendation of chlorine residuals of 0.002 mg/l or less for the protection of most aquatic organisms causes a dilemma in relation to the use of chlorine as a disinfection agent in municipal sewage treatment. One one hand, disinfection is necessary to remove potentially hazardous micro-organisms; conversely, the presence of chlorine at disinfection levels can be toxic to some species present in the receiving waters. The problems specifically involved with Fields Brook are the accurate determination of free versus combined chlorine residuals and the determination of chlorine demand and degassing parameters. A theoretical model has been developed as part of this effort and is presented here (Pereira, Terlecky and Yaksich, 1974) as Appendix 3. The method used in this investigation was the orthotolidine method for determination of total residual chlorine concentration. Because of the absence of any appreciable amount of ammonia present in Fields Brook waters and because of large quantities of chlorine added to the water, all of the ammonia should be oxidized at the pH values encountered. Normally 8 to 10 parts of chlorine per part of ammonia nitrogen are required to remove all of the ammonia at what is called the breakpoint. Excess chlorine remains as free chlorine. Fields Brook, with low ammonia values and high total residual chlorine values, thus should have high values of free residual chlorine in relation to combined residual chlorine. The model developed in Appendix 3 thus would be directly applicable to the Fields Brook situation. Based on the average amount of ammonia present in Fields Brook and total residual chlorine values measured, it is estimated that as much as 80 to 90% or possibly more of the total residual chlorine is actually free chlorine. Residual chlorine values present in Fields Brook clearly have an important effect upon biota associated with it. Vegetation which is near the brook is brown and mottled in appearance. At many places, most of the vegetation is dead. Station 2, Fields Brook had very low planktonic cell counts and had a relatively low diversity of organisms present during plankton collection.

Most of the organisms (plankton) found in the Fields Brook samples were alive when collected which suggests being washed in from upstream Fields Brook areas above the major chlorine discharge (and thus above Station 2) since tolerance of chlorine levels measured here would not be expected. Flow velocities in Fields Brook exceed 2 feet per second which reduces exposure time. Throughout this study, cell counts of planktonic organisms were low in Fields Brook confirming the presence of postulated toxicity conditions. Because of the levels of chlorine discharged from Fields Brook, and the presence of residual chlorine concentrations above the recommended levels, it is relatively safe to conclude that continued discharge of chlorine from Fields Brook at the levels measured in this study causes the deterioration of water quality from the Penn Central Bridge to the entire harbor area.

Several options are available for control of the chlorine discharges. Sulfur dioxide or sulfite treatment is well known and has been proven to be effective in reducing the chlorine toxicity of wastewaters.(See, for example, Baker, 1964; White, 1968; White, 1972, p. 456; Dean, 1974). Lagooning, pH control between 7 and 8, and retention for a very few minutes should be sufficient to control chlorine levels to tolerable levels. Injection of SO_2 or sulfite in the wastewater in sufficient quantities to reduce residual chlorine levels to tolerable limits in the range of 1-.5 mg/l at the State Road outfall on Fields Brook should be sufficient to preclude harmful effects to resistant aquatic biota in the Ashtabula River. Other dechlorination methods available include activated carbon (White, 1972; Bauer and Snoeyink, 1973) and ammonia (White, 1972). Each method has its own limitations which must be explored fully for application to a specific case.

A second option which should be examined is the piping of all or part of the chlorine-containing effluent to the municipal sewage treatment plant, a distance of approximately one mile. The possible utilization of this wastewater might therefore eliminate two problems. The purchase of chlorine by the treatment plant and the elimination of a harmful effluent from Fields Brook. Undoubtedly, there are many serious facets to this solution which must be explored to determine feasibility, but consideration of this appealing option should be made.

The presence of many chlorinated organic compounds previously suspected as possibly being present in Fields Brook waters was not confirmed in this study. Phenol levels also were quite low. Therefore, the reactions which might be suspected to take place in Fields Brook between chlorine and other organic compounds were not detected.

Examination of the empirical data for Fields Brook, and the Ashtabula River and Harbor area for total chlorine residuals enables an estimate to be made of what levels of control might be necessary to reduce chlorine concentrations to acceptable levels. It should be borne in mind that these estimates are empirical estimates and should be used only as indicators rather than absolute guidelines. Table 40 was constructed to assemble available chlorine data for key stations and facilitate this empirical estimate. A sample of the outfall on the west side of the State Rd. bridge over Fields Brook indicated the presence of 35.0 mg/l total residual chlorine concentrations (5/10/74). The maximum amount of discharge allowed for this period by NPDES permits issued by the USEPA was 25 mg/l for one company in the Fields Brook area.

Levels of residual chlorine concentration of 3-12 mg/l at the E. 15th St. sampling location and Fields Brook may represent values of from appoximately 30 to greater than 100 mg/l at the upstream outfall in the absence of diluting waters. A reduction of total residual chlorine concentrations at the State Rd. outfall at least to 0.5-1 mg/l thus appears necessary to reduce concentrations

Table 40

TOTAL CHLORINE RESIDUAL (mg/ℓ) MEASURED AT SAMPLE SITES ON DIFFERENT DATES

Date	9/5/73	9/8/73	9/10/73	5/8/74	5/8/74	5/9/74	5/9/74	5/10/74
Station Outfall on Fields Brook	-	-	-	-	-	-	-	35.0
2	12.0	1.10	6.5	6.5	4.5	4.5	3.0	2.4
Mouth of F.B.	-	-	-	9.5	4.0	3.0	3.0	-
3	0.05	0.01	0.02	-	-	-	-	-
4	0.04	<0.01	0.01	-	-	-	-	-
5	0.01	0.01	0.01	-	-	-	-	-
8	0.005	-	-	-	-	-	-	-
6	< 0.005	0.01	<0.01	-	-	-	-	-

at the Fields Brook mouth to 0.1 mg/l, a value which should protect resistant species in the Ashtabula River. Such reduction would also reduce levels in the lower river and harbor to values of 0.01 and less during low flow periods. Present measurements vary from 1-5 mg/l commonly at the mouth of the brook. This value is highly variable depending upon runoff, sunlight, and initial concentration in the outfall. Clearly if the use of empirical measurements is valid in this case, it will be necessary to drastically reduce Fields Brook chlorine residuals from present levels to protect river and harbor biota. During periods of relatively high flow of the river (discharge in excess of 150-200 cfs), the permissable limits of discharge can be set higher. No reduction of Fields Brook chlorine residuals was seen during the May 1974 sampling period, a period during which the new NPDES permits have been in effect. One discharge source is known to contribute wastewater of a total residual chlorine value as high as ≈200 mg/l at various times. This source is expected to be under permit at the end of 1974.

A detailed monitoring program for chlorine concentrations appears warranted, therefore, to quantitatively determine empirically what relation outfall values have to values in Fields Brook, the Ashtabula River, and Ashtabula Harbor. Based on the above data, it is necessary to reduce values at the Fields Brook mouth to .1 mg/l total residual chlorine to insure protection of resistant species in the Ashtabula River. For protection of less resistant species, further reduction of values measured in the Fields Brook mouth to <.05 mg/l will be necessary. The only definite way to insure that these values are attained is to significantly reduce discharge limits of total residual chlorine to at or below those recommended for attainment at the State Road outfall. In this way, variations in flow rates and other conditions can be accommodated.

Dissolved Solids and Conductivity

Examination of conductivity data as an index to dissolved solids concentrations, plus the data obtained by direct measurement in the primary sampling series of this study leads to the conclusion that one of the prime deterents to improved water quality is the presence of large amounts of dissolved solids. Because of the nature of the industries located on Fields Brook, this observation could be expected.

Total dissolved solids content of Fields Brook ranged from 1495 to 1612 mg/1 at Station 2 during the primary sampling. Examination of the conductivity profile presented in Figure 4 clearly shows the source of dissolved solids in the study area. Because of the large amount of dilution in the lower river and harbor area, lake levels are exceeded only slightly. Therefore, the major effect of large dissolved solids concentrations entering the river from Fields Brook are seen approximately one-half mile upstream and one mile downstream. Biota differences in the study area will be discussed later, but the presence of dissolved solids at these levels (with approximately one-third represented by chlorides) must affect the character of the biota inhabiting this portion of the river. Data in the literature do not appear definitive as to the effect of dissolved solids on biota. Forms tolerant of high dissolved solids concentrations might be present because the concentrations at these levels will affect the osmoregulatory organs of the organisms. The chief effect upon fish and other higher forms may be to prevent them from inhabiting the area because of avoidance. Planktonic forms not adaptable to dissolved solids at these levels simply will not survive during periods of low river flow.

Flushing Time

Flushing time has been reported on the basis of data presented in Section 5 of this report for Ashtabula Harbor during the period 9-11 May 1967. There are many factors which complicate the rather simplified method and might cause the results to be viewed as estimates rather than precise figures. In the absence of a superior method, The Army Corps of Engineers method was applied to this case. The concentration of the sodium ion was measured at many stations and depths in the river and harbor in order to enable a calculation of the volume of river water present in the harbor at any one time.

The values used for the calculation were as follows (average values for 5, 8, 10 September 1973):

S_o = sodium concentration in harbor = 21.2 mg/l

S_n = sodium concentration in lake = 15.3 mg/l

S_r = sodium concentration in river = 108.6 mg/l

V_r = % of river water in harbor

Using the method presented in Section 1,

$$V_r = \frac{100(S_o - S_n)}{S_r - S_n}$$

$$V_r = \frac{100\ (21.2-15.3)}{108.6-15.3} = 6.32\%$$

Therefore, 6.32% of the water in the harbor was river water according to this calculation (low flow conditions). Discharge of the Ashtabula River during the sampling days average 1.57 cubic feet per second or 135,648 cubic feet per day. The total volume of the harbor at L.W.D.*is $294{,}270 \times 10^3$ cubic feet.

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*Low Water Datum was used because the volume of the harbor was previously determined by the Army Corps of Engineers (1968).

Flushing time was then computed from the relationship:

$$\text{Flushing Time} = \frac{V_r}{Q} = \frac{.0632\ (294{,}270 \times 10^3)\ ft^3}{135{,}648\ ft^3/day}$$

$$= \frac{18597.86 \times 10^3\ ft^3}{135{,}648\ ft^3/day}$$

$$= .1371 \times 10^3 = 137.1\ \text{days}$$

Assuming a flow of river discharge along a path 1,200 feet wide (the dredged channel) from the river mouth to the harbor entrance, and further assuming that 80% of the river flow followed this path*, the Path Flushing Time was computed at 60 days.

To view this in perspective, the following table was constructed to illustrate the conditions which the flushing time calculations represent:

	9-11 May 1967	5, 8, 10 Sept. 1973
Discharge of River	586 ft^3/sec	1.57 ft^3/sec
	50,630 X 10^3 ft^3/day	135.6 X 10^3 ft^3/day
Volume of River Water in Harbor	44%	6.32%
Harbor Flushing Time	2.83 days	137.1 days
Path Flushing Time	1.24 days (29.8 hr)	60 days

Examination of this data illustrates the problem facing the Ashtabula Harbor area with receipt of concentrated discharge during periods of low flow

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[*] Following ACE methods (ACE, 1968), the remainder would leave the harbor by flowing to the East around the East breakwater.

which are typical for the Ashtabula River during late Summer and early Fall. With very little inflow of water, there is very little water available for dilution of wastes. Therefore, dilution must occur with harbor or lake water. These calculations can be viewed as conservative, i.e., that they do not take into account wind and current effects, circulation patterns in the harbor and the effluent wastewater volume. Discharge as expressed here is Ashtabula River discharge. Therefore, during the annual minimum flow of the river, essentially the vast majority of the river flow to the harbor is waste effluent from the Ashtabula industrial complex through Fields Brook. The water present in the harbor, however, is lake water for the most part during low flow periods. Chemical data which illustrate Fields Brook influence extending upstream to the Penn Central Bridge (Station 1) substantiate this conclusion. High concentrations of conductivity, chloride, and on one occasion mercury have been measured at this upstream station indicating the basically stagnant nature of the river and harbor areas during low river flow.

Biota Aspects

Historical vs. Present Biota

A variety of methods commonly used to express the abundance of zoo - and phytoplankton makes comparison of present data with historic data difficult. Phytoplankton data, for instance, have been presented as volume per unit volume of water (State of Ohio, 1953), dominant category in percent-of-total phytoplankton population (FWPCA, 1968; Reitz, 1973), total cells per unit volume of water without reference to species present (Reitz, 1973; Davis, 1964,11965), or simply the genera, and sometimes the species, of organisms present (Davis, 1962; Verduin, 1960; Metcalf, 1942).

Species of phytoplankton recovered from Station 6 (Lake Erie outside the harbor) were not the typical dominant lake species normally expected based on available literature, although none were foreign to Lake Erie water samples. Diatoms have always dominated Lake Erie phytoplankton populations; however, important chlorophytes reported have included *Pediastrum simplex*, *Closteriopsis longissima* and *Staurastrum*. Dinophytes commonly recorded in high concentrations were *Certium hirundinella*. Cyanophytes common to Lake Erie included *Anacystis.*

Typically, *Asterionella formosa* dominated Lake Erie water until 1950, when *Melosira* became the most frequently recovered diatom. *Cyclotella* rose to prominence during the 1960's, included at least four important species. *Fragilaria* has been a dominant component of all lake samples and all seasons. *F. capucina* and *F. crotonensis* were most prevalent in samples prior to this study.

The data reported here for 1973 however isolated high concentrations in Lake Erie in *F. virescens* and *F. crotonensis* (60-65%) of total. Seasonal variations in diatom populations may explain the absence of *Asterionella* from lake and harbor samples obtained in late summer, as *Asterionella* might be expected to reach its peak in the spring. *Melosira*, however, would be expected in samples from all seasons, but was, in fact, absent or in low concentrations (0-12%) in September, 1973. *Cyclotella*, which had been isolated as a dominant diatom frequently in previous Lake studies (Huntz, 1954, 75-79%; McQuote, 1954; Wujek, 1967, Detroit River; Verduin, 1962; Davis, 1954), was found to comprise only 4% of mid-depth samples, but 15% of bottom samples, sharing the dominant position at 12.8 meters with *Tabellaria fenestrata* (14%), *Melosira* (12.5%), *Stephanodiscus* (12.5%) and *Fragilaria* (11.5%).

Zooplankton historically have been a minor component of lake plankton samples and have included cladocerans (*Daphnia*), copepods (*Diaptomus*) and rotifers (*Keratella*). Only *Keratella cochliaris* was recovered in significant proportions in lake samples during this study, although *Codonella* and *Diaptomus* were in evidence in mid-depth and bottom samples only.

Benthic organisms from Lake Erie near the Ashtabula River have traditionally included tubificids, molluscs (pelecypods and gastropods), dipterans (*Chironomus*), leeches and nematodes (ACE, 1968; Brown, 1953). Samples dredged during the present study contained very few tubificids (approx. 150 per m^2) and approximately 50 tiny *Sphaerium* (clams) per m^2. Toxic silts deposited by the river flow may cause loss of diversity and lack of abundance in benthic populations. Previous work has indicated that quantities of potentially toxic metals deposited in the sediments of the river and harbor area annually reach 112 pounds of mercury, 2,534 tons of iron, 14 tons of chromium, ≈28 pounds of cadmium, ≈56 pounds of arsenic, 22 tons of zinc, ≈11 tons of lead, 3 tons of copper and 1 ton of nickel (Leonard, 1972). In 1967, *Peloscolex* comprised 4-6% of benthic populations located in or near the dredgings dump ground (ACE, 1968). The concentration of populations of *Peloscolex* and *Pisidium* (clam) increased in the lake, as distance from possible toxic situations increased. In 1973 samples from this survey, however, neither organism could be found in Lake Erie samples outside Ashtabula Harbor.

The Ashtabula River and Harbor have historically contained similar biological communities though the harbor has a nutrient rich environment. Plankton concentrations (State of Ohio, 1953) in lake and harbor water were $8.48 \times 10^8 \mu^3$ and $4.27 \times 10^8 \mu^3$ respectively, but populations consisted of similar organisms and in the same order of dominance: *Melosira*, *Stephanodiscus*, *Fragilaria*, and *Asterionella*.

1973 studies indicated a fairly diverse environment in harbor and lower river waters, but cell concentrations had followed a trend of declining abundance. Surface samples from the harbor were more diverse in species than surface water from the river at Station 3, though the communities were similar in dominant species. *Closteriopsis longissima* dominated in the river, but dropped to a much lower position in harbor communities, where *Anacystis*, a blue green Algae, appeared, though not in significant concentrations.

Diatom communities were not similar between harbor and lower river samples. Harbor communities were similar to those reported for 1950, except that *Cyclotella* has emerged as a prominent species and *Asterionella* was not recovered. *Melosira* has declined in abundance also, so that *Cyclotella*, *Stephanodiscus*, *Fragilaria virescens*, *F. crontonensis*, and *Coccinodiccus* comprise 58.8 (bottom) to 72.4% (surface) of the community.

Benthic organisms from mid-harbor resembled 1950 and 1967 collections: tubificids, leeches, and clams, except that studies in 1967 (ACE,1968) had recovered a more diverse community including *Peloscolex*, *Amnicola* and *Chironomus*. As in previous studies, the harbor benthos was more diverse than river benthos. River benthos included approximately 5750 immature tubificids per m^2. No other organisms were recovered. Harbor tubificids numbered 2500 worms per m^2. The greater number of species recovered indicates the harbor is a healthier benthic environment than the Ashtabula River below Fields Brook.

Prominent lower river diatom species also support this conclusion. *Cyclotella*, *Nitzschia*, *Navicula* and *Synedra* are highly rated as pollution tolerant (Palmer,1969).

No previous historic data on the biota of Fields Brook and the upper Ashtabula River could be located, therefore, comparisons of biota upstream of Station 1 in this study to previous studies cannot be made.

Relationship of Water Chemistry to Biological Communities

In estimating the level of pollution, biological communities are frequently used to evaluate the quality of the environment. Diatoms and other phytoplankton may indicate the level of organic pollution, pH differences, or the eutrophic state of the water. Benthic organisms, such as the abundance of various tubificid species or the diversity of communities, may indicate the extent of organic pollution or the toxic metal content of sediments. In general, the phytoplankton in the Ashtabula River area did not include blooms of individual species or an abundance of blue green algae, which might be expected in late summer. This did not indicate favorable water quality, but instead, pollution-tolerant organism groups present, relatively low diversity and low concentrations of plankton cells in the River-Harbor-Lake area indicate a toxic situation in which the biota are severely inhibited. In view of the previous discussions of low cell counts encountered in this study, it could be concluded that smaller forms escaped the plankton net. However, larger forms present (>100µ) and diatoms (sampled without the use of a net) were also found to be present in unusually low numbers confirming the importance of toxic substances in inhibiting suitable environmental conditions for high diversity and high cell numbers.

Station 3 was chosen to show the influence that Fields Brook contaminants may have on biological communities downstream. Plankton analyses showed few species present. Cell numbers were also extremely low, with only a few species dominating. Water conditions, chemically, were poor due to influence of Fields Brook water which carried high concentrations of chlorine, dissolved solids, mercury, other metals, and chlorides into the river above Station 3. The results of the unfavorable addition of contaminants have been to reduce dissolved oxygen concentrations, produce high dissolved solids concentrations, to elevate chloride and chlorine concentrations. The water has been further degraded by sanitary sewage input directly to the river at certain points by private sources.

This has resulted in elevated fecal coliform concentrations. The turbidity of river and harbor waters may have had serious effect on phytoplankton growth.

The result of dilution of these contaminants by river flow and in harbor waters can be seen by an improvement in diversity and abundance of biota in the mid-harbor samples. Benthic conditions were improved, as well as the planktonic biota of harbor water, over that observed in the river, where only tubificids could be found.

Lake Erie water samples also contained inhibited populations of plankton and benthos, especially diatoms in surface waters, which were extremely scarce. This finding does not agree with previous reports of Lake Erie plankton concentrations in this area and would, therefore, indicate a toxic influence of water from the Ashtabula River and Harbor on Lake Erie water outside the harbor breakwalls. This conclusion should be confirmed by a more detailed biological study.

Section 8
PRESENT AND FUTURE IMPACT OF DISCHARGES ON WATER QUALITY AND BIOTA

Current Impact

Examination of the previous two sections of this report indicates the major problem areas for Fields Brook and therefore Ashtabula River water quality:

1. Control of chlorine discharges
2. Control of mercury discharges
3. Control of dissolved solids discharges

Solution of these three problems should eliminate the vast majority of water quality-related adverse effects. Although with the exception of one sampling instance, the purpose of this study was not to sample effluent from individual plants, measurement of water quality at selected positions along Fields Brook and the Ashtabula River enable conclusions to be drawn concerning upstream, and thus effluent water quality.

The impact of present discharges on the water quality and biota of the Fields Brook and Ashtabula River area has been discussed in Section 3 and 4 of this report. Significant changes in water quality and the biota of the area have occurred since 1950, and as this study shows, continued through 1973 and early 1974. To date (Summer 1974), permits issued by the USEPA after public hearings in Ashtabula have made no significant impact in improvement of water quality in Fields Brook and the lower river as far as the critical parameters enumerated by this study are concerned. Slight improvement in the river and harbor areas has been detected but it is not known whether this is caused by reduction of effluent or the high water levels (and thus dilution) of the past two years. The organic loading of Fields Brook is low. Relatively low values of COD, BOD and TOC attest to the capability of current permit levels to control discharges which would influence those parameters. Nitrate values for Fields

Brook, at least during late 1973, remained at levels which act as a nutrient source for phytoplankton and algae. No limitation has been placed on nitrates. Temperature limitations at this writing have not been imposed on the Fields Brook industries. We conclude from examination of Fields Brook temperature conditions that thermal limitations should be imposed, particularly with reference to cooling water discharges. During the May sampling period, the discharge entering the turning basin from the west side was red in color after a short rainfall. A scrap yard further up the drainage ditch appeared as the possible source of the rust-colored particulates or suspended matter.

Fields Brook water quality as far as chlorine residuals, mercury concentrations and dissolved solids content are concerned has not improved. In fact, during the low flow period of the primary sampling period, conditions appeared to worsen. On one sampling day, reports of people being overcome by chlorine fumes the previous night were relayed by local people. Hearings held on October 30,1973 confirmed this.

In summary, water quality conditions in Fields Brook for the period October 1973 to April 1975 could be expected to improve if the issued permits were complied with, but the data show that the level of chlorine and mercury residuals in Fields Brook, even after dilution by natural water, exceed the maximum levels allowed in any of the NPDES permits. There is no doubt therefore that current compliance with the existing permits is not complete as far as Fields Brook as a whole is concerned. Other less crucial parameters such as temperature, metals, and minor organic contributions are expected to improve slightly.

Predicted Future Impact

If the terms of the permits for the period 1975 to 1978 were complied with, the data gathered here indicate that significant improvement of water quality can be expected in a short period of time in Fields Brook. The maximum total residual chlorine allowed after April 1975 would be 0.3 mg/l at each outfall for existing NPDES permits. One permit for a chlorine discharging facility has not been granted at this writing. The draft permit, however, currently has a 0.3 mg/l limitation for total residual chlorine to be met by July 1,

1977. Reduction of chlorine concentrations to this maximum level above (and 0.1 mg/l average) should result in the lowering of Fields Brook total residual chlorine levels to the range 0.05-0.005 mg/l at the Fields Brook mouth. Chlorine demand parameters present in Fields Brook such as the presence of ammonia (forming chloramines) and metals would further reduce the toxicity of this discharge and complex the available chlorine.

The control of mercury discharges in the parts per billion range is an extremely difficult procedure by standard methods. Because of the State of Ohio standard of 0.5 μg/l (.5 ppb), it appears that either total recycle, routing to another receiving water body, or the segregation and treatment or extraction of mercury and source discharges must be considered. Recent advances in mercury discovery from wastewater and sludges may provide methods useful for removal of the mercury at its source (Perry, 1974). An additional possibility would be use of a different method or type of electrode for sodium and chlorine manufacture.

There appears to be no demonstrated technology for the large scale removal of dissolved solids. The permits granted to the Fields Brook industries indicate that no relief is in sight for the dissolved solids concentrations in Fields Brook and thus the Ashtabula River. Levels as high as 5000-6800 mg/l as an average are allowed by current permits.

Suspended solids concentrations as measured in this study do not reveal a major problem. Other data that exist suggest that a problem does indeed exist. A more extensive sampling program seems required to define its extent. Suspended solids concentration in cooling water obtained from Lake Erie may at times reach levels as high as 200 mg/l or more as a result of natural phenomena. The discharge of this cooling water into Fields Brook certainly increases suspended solids concentration in that stream. Compliance with permits therefore, would cover suspended solids concentrations in Fields Brook. Perhaps the greatest source of water exchange during periods of low flow in the Lower Ashtabula River and Harbor is lake setup and wave action.

During periods of high natural suspended solids in the lake (maximum setup and wave action), the natural suspended solids concentration of lake water would control suspended solids in the harbor and lower river. Compliance with permits therefore would have little effect in these reaches.

The technology to remove suspended solids by settling and floculation is available and can be applied to attain the final limitations mandated by the permits. If the permit levels are attained, a definite improvement in suspended solids content can be expected in Fields Brook. No control is available for Lake Erie, however, and it is well known that lake effect extends upstream to the Penn Central Bridge.

If reduced to permit levels, the lowered metals concentrations of Fields Brook discharges should serve to improve water quality with respect to these parameters. Lower concentrations of cadmium, copper, nickel and lead required by the new permits, will contribute to improved conditions for biota in the lower river. The chief effect of the permits in this area should be to lower the levels of metals deposited as part of the sediments in the study area. This will improve bottom conditions and be more conducive to more desirable benthic populations.

Recycling process water should be considered by the industries as a possible solution to metals discharge, particularly mercury. The piping of chlorine containing wastewater to the Ashtabula municipal sewage treatment plant for mixing with the STP effluent may provide a solution for removal of at least part of the chlorine residual problem. Temperature limitations have been ignored on present permits and should be reexamined in light of elevated temperatures present throughout the year in Fields Brook.

In summary, permit limitation levels with respect to chlorine and mercury levels do not appear to be met at present. If the discharges are reduced to permit levels in 1975, significant improvements in water quality can be expected to occur. The important factor appears to be compliance with the permits, and, in cases of non-compliance, prompt enforcement action.

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APPENDIX 1.

Methods of Analysis for the Ashtabula Ohio Water Quality Analysis (A = "Methods for Chemical Analysis of Water and Wastes," B = Standard Methods for the Examination of Water and Wastewater," 13th ed., 1971)

Parameter	Reference	Page	Method#
Temperature	B	559	162
Hardness	B	179	122A
Alkalinity	A	6	
Conductivity	A	284	
Dissolved Oxygen	A	53,60	
BOD_5	B	489	219
BOD_{20}	B	489	219 (20 days)
COD	B	495	220
TOC	A	221	
Solids (Settleable)	B	539	224F
Solids (Suspended)	B	537	224C
Solids (Dissolved)	B	539	224E
Solids (Total)	B	535	224A
Coliform (Total)	B	679	408A
Coliform (Fecal)	B	684	408B
Phosphorus (Total)	A	242	
Phosphorus (Ortho)	A	235	
Ammonia	A	134	
Kjeldahl Nitrogen	B	458	213B
Nitrate	B	469	216
Phenols	A	232-233	
Cyanide	A	41	
Chloride	A	29	
Fluoride	A	64	
Sulfate	A	286	
Chlorine (Total Residual)	B	117	114C
Oils and Grease	A	217	

APPENDIX 1 (Cont'd)

Methods of Analysis for the Ashtabula Ohio Water Quality Analysis

(A = "Methods for Chemical Analysis of Water and Wastes," B = Standard Methods for the Examination of Water and Wastewater," 13th ed., 1971)

Parameter	Reference	Page	Method#
Organochlorine Pesticides	Methods for Organic Pesticides in Water and Wastewater, EPA 1971 (also Federal Register V. 38, #125, 29 June 1973 App. II)		
Organics	Extraction with suitable solvent and gas chromatographic techniques employing flame ionization detection and electron capture detection		
Arsenic	B	62	104A
Barium	B	210	129A
Cadmium	A	83	
Chromium	A	83	
Copper	A	83	
Iron	A	83	
Mercury	A	121	
Nickel		Atomic Absorption	
Lead	A	83	
Selenium	A	296	150A
Titanium		Atomic Absorption	
Zinc	A	83	

APPENDIX 2
GENERAL STANDARDS OF WATER QUALITY FOR OHIO STREAMS

	mg/l	µg/l
Ammonia	1.5	--
Arsenic	--	50
Barium	--	800
Cadmium	--	5
Chloride	250	--
Chromium	--	300
Chromium (hexavalent)	--	50
Cyanide (Free)	.005	--
Cyanide (Total)	0.2	--
Fluoride	1.3	--
Surfactants (MBAS)	0.5	--
Iron (Dissolved)	--	1000
Lead	--	40
Manganese	--	1000
Mercury	--	.5
Oil and Grease (hexane ext.)	5	--
Phenols	--	10
Selenium	--	5
Silver	--	1
Copper	--	75-500 (varies with hardness)
Zinc	--	5-75 (varies with hardness)
Phosphorous (Total)	(limited to prevent nuisance growths always ≤1 mg/l daily ave. in nuisance growth areas)	
Total Dissolved Solids	may exceed one but not both: 1500 mg/l, 150 mg/l	
Dissolved Oxygen	≥5.0 mg/l (daily ave.); ≥4.0 at all times	
Fecal Coliform	≤200/100 ml - 30 day geom. mean ≤400/100 ml in 20% or less of samples	

Temperature	5°F (2.8°C) over ambient with max. limits set forth in a table in para. G, EP-1-02
Radioactivity:	
Gross Beta	≤100 picocuries/liter
Strontium 90	≤ 10 picocuries/liter
Alpha emitters	≤ 3 picocuries/liter

APPENDIX 3

On November 17, 1972 Cornell Aeronautical Laboratory (CAL) changed its name to Calspan Corporation and converted to for-profit operations. Calspan is dedicated to carrying on CAL's long-standing tradition of advanced research and development from an independent viewpoint. All of CAL's diverse scientific and engineering programs for government and industry are being continued in the aerosciences, electronics and avionics, computer sciences, transportation and vehicle research, and the environmental sciences. Calspan is composed of the same staff, management, and facilities as CAL, which operated since 1946 under federal income tax exemption.

THE PREDICTION OF FREE RESIDUAL CHLORINE CONCENTRATIONS IN A FLOWING STREAM

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Calspan Report No. ND-5358-M-1

Prepared For:

U.S. ENVIRONMENTAL PROTECTION AGENCY
REGION V, ENFORCEMENT DIVISION

30 JANUARY 1974
CONTRACT NO. EPA 68-01-1575

Calspan Corporation
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ABSTRACT

Chlorine use for disinfection and as an antifouling agent, as well as its presence as a product of industrial processes has resulted in possible toxic effects to aquatic biota. A model which predicts free residual chlorine concentrations is developed here which considers hydrodynamic transport, chlorine demanding reactions, and gaseous exchange with the atmosphere in a flowing stream. The mathematical expression of the model is written as:

$$\frac{\partial C_F}{\partial t} = E \frac{\partial^2 C_F}{\partial x^2} - U \frac{\partial C_F}{\partial x} + r_C + r_E$$

This expression thus expresses the rate of change of free residual chlorine concentration as a function of turbulent diffusion, convective motion, chlorine demand and gaseous escape. A method is also suggested by which parameter values may be obtained from laboratory and field experiments for use in the model.

ACKNOWLEDGMENT

The authors wish to thank Mr. Howard Zar (Region V Enforcement, USEPA) and Mr. Gary Amendola (USEPA, Cleveland) for suggestions on the possibility of modeling chlorine and discussions leading to the initiation of this paper. Thanks are also due to Mr. John Michalovic also of Calspan for technical suggestions and discussions on various parts of this report.

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Section 1.
INTRODUCTION

The widespread use of chlorine for disinfection, and the high chlorine concentrations in the effluents of various manufacturing processes, leads to a concern for the potential adverse effects of residual chlorine on aquatic organisms.

Data have become available on the levels of toxicity of chlorine to several fish species, phytoplankton and zooplankton (Brungs, 1973; Brook and Baker, 1972; Hamilton *et al.*, 1970). In general, recommended disinfection concentrations are between 0.5 and 1.0 mg/l which is well below known toxicity levels to mammals (Muegge, 1956; Brungs, 1973); however, concentrations not to exceed 0.002 mg/l (applied continuously) have been recommended for the protection of most aquatic organisms (Brungs, 1973). Chlorine has been used for swimming pool disinfection, municipal water supplies, sewage disinfection, industrial waste treatment, and many other uses. Chlorine is commonly used for prevention of algal and slime growth in cooling towers (Nelson, 1973; Brook and Baker, 1972; Hamilton *et al.*, 1970; Beauchamp, 1969; Sladekova, 1969), as well as an antifouling agent for water conduits and intakes (Turner *et al.*, 1948; Hamilton *et al.*, 1970).

The presence of high concentrations of residual chlorine in effluent produced as a result of several industrial processes is well known. The following processes are among those which may contribute to high residual chlorine values in wastewater:

(1) Electrolytic decomposition of molten sodium chloride.

(2) Electrolysis of HCl acid to yield H_2 and Cl_2 as a recovery operation.

(3) Electrolysis of brine.

(4) Production of chlorates for bleaching paper.

(5) Production of sodium hypochlorite for laundry bleaching.

(6) Paper and pulp manufacture.

Thus, the widespread use of chlorine and the presence of chlorine discharges in the nation's water bodies require close scrutiny. In order to prevent and control potentially toxic discharges, it is important first to understand the relation between a specific discharge into a water body and its ultimate effect upon the quality of that water. If the cause-effect relationships are known, then the effectiveness of prospective control programs can be better evaluated. This cause-effect relationship can be expressed in the form of a mathematical model where each known step or process is represented by a corresponding mathematical analog. The better each step is understood, and the more accurate its consequent translation into a mathematical analog is made, the more reliable the mathematical model will become. A rigorous comparison must also be made between the model and actual data before the model can be used in a predictive capacity.

The objectives of this study are to:

(1) Develop a mathematical model which predicts free residual chlorine in a flowing stream. The model will incorporate time and position variables, concentrations, and will be based upon actual process mechanisms.

(2) Design an experimental procedure to verify the model.

As in any quantitative work under field and laboratory conditions, it is necessary to make some assumptions about the problem or impose some limitations on the generality of the results before analysis can begin. Implicit in the development of the model are the following assumptions and limitations:

1) The analysis is restricted to a one dimensional macro-scale system.

2) Specific functional forms are assumed to describe the dynamic behavior of the chemical components and physical conditions of the model. An effort is made to accurately reflect the actual process mechanisms while not overcomplicating the model.

In regard to the chemical considerations, it must be remembered that chlorine is a powerful oxidizing agent which will react chemically with inorganic reductants as ferrous, manganous, nitrite, and sulfide as well as organic materials. Since a large number of water borne materials can consume chlorine, any attempt to model individual chemical reactions would soon become overwhelming. As in the case of oxygen, the behavior of chlorine in a given water body can be more easily described if the materials which consume chlorine are thought to exert a chlorine demand just as materials which consume oxygen are thought to exert an oxygen demand. Therefore, when attempting to verify a chlorine model based on chlorine demand, one of the parameters that is needed is the chlorine demand of the water. Measurement of parameters which consume chlorine such as BOD, COD, phenol, organic and ammonia nitrogen, iron, and manganese as are available from the data on Fields Brook[*] will not be suitable to verify this model.

Chlorine in water may be present as free available chlorine in the form of hypochlorous acid or hypochlorite ion or both. Chlorine may also be present as combined available chlorine in the form of chloramines and other chloroderivatives. However, free available chlorine is more toxic and its effect is more rapid than that of combined available chlorine. Therefore, this paper emphasizes the behavior of free available (residual) chlorine.

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[*] Ashtabula, Ohio.

If this approach to model the movement and consumption of chlorine in a stream later proves to be too simplistic, other process mechanisms may be incorporated into the model as needed.

Section 2.

DEVELOPMENT OF THE MODEL

The movement and reactions of chlorine through a stream is a resultant of hydrodynamic transport within the stream, gaseous exchange with the atmosphere, and biological and chemical reactions. These relationships can be expressed by a mathematical model which reflects the various inputs and outputs in the aquatic system. Considering the free residual chlorine balance in a one dimensional flowing stream, the following second order partial differential equation which was used in the development of a dissolved oxygen model is applicable (O'Connor, 1967):

$$\frac{\partial C_F}{\partial t} = E \frac{\partial^2 C_F}{\partial x^2} - U \frac{\partial C_F}{\partial x} \pm S \qquad (1)$$

where:

C_F = Concentration of free residual chlorine (mg/l)

t = Time at a stationary point in the stream (sec)

U = Flow velocity in the x direction (m/sec)

E = Stream diffusion coefficient in the longitudinal direction (m^2/sec)

x = Distance downstream (m)

S = Sources and sinks of free residual chlorine (mg/l/sec; chlorine demand, gaseous exchange, etc.)

The one-dimensional assumption of equation (1) implies that the concentration is uniform over the stream cross-section. The concentration of free residual chlorine in the incoming or tributary flow is considered the initial condition C_{FO} in equation (1).

The Chemical System

The chemical behavior in a given water body is very complex and physical factors affect any given constituent. This is especially true in the case of chlorine, a powerful oxidizing agent with a high solubility in water. The following equilibrium equations are obtained when elemental chlorine is dissolved in water (Fair et al., 1968; Connick and Chia, 1959):

$$\text{Hydrolysis:}\quad Cl_2 + H_2O \rightleftharpoons HOCl + Cl^- + H^+ \qquad (2)$$

$$K_h = \frac{(HOCL)\ (Cl^-)\ (H^+)}{(Cl_2)} = 4.5 \times 10^{-4}\ (\text{moles}/_{\text{liter}})^2 \text{ @ } 25^oC$$

$$\text{Ionization:}\quad HOCL \rightleftharpoons H^+ + OCl^-$$

$$K_i = \frac{(H^+)\ (OCl^-)}{HOCl} = 2.7 \times 10^{-8}\ \text{moles}/_{\text{liter}} \text{ @ } 25^oC \qquad (3)$$

White (1972) reports, as a result of a tabulation of data of several investigators, that the hydrolysis constant has been determined with substantial agreement along investigators and is of the value 3.9 to $\approx 4.5 \times 10^{-4}$ (moles/liter)^2. The hydrolysis constant K_h is of such magnitude that free chlorine does not usually remain in solution at pH values greater than 3 and total chlorine concentrations of less than 1000 mg/l (White, 1972). At normal water temperatures, the hydrolysis of chlorine is essentially complete within a few seconds, and the ionization of hypochlorous acid produced is in essence an instantaneous reversible reaction (Fair et al., 1968). The ionization constant, K_i, is a function of temperature (Fair et al., 1968).

The free residual chlorine, normally referred to , is that portion of the total residual chlorine which will react chemically and biologically as hypochlorous acid or hypochlorite ion (Standard Methods, 1971). Consequently

$$C_F = (HOCl) + (OCl^-)$$

$$= (HOCl) + \frac{(HOCl)\ K_i}{(H^+)}$$

i.e.

$$C_F = (HOCl)\left[\frac{(H^+) + K_i}{(H^+)}\right] \qquad (4)$$

In the above equation (4), it is assumed that the HOCl and OCl^- are in equilibrium and the equilibrium relationship from equation (3) is used to relate the free residual chlorine concentration C_F to the pH, K_i and the hypochlorous acid concentration.

The consumption of the free residual chlorine is referred to as the chlorine demand. The chlorine demand of a particular water body is caused by such inorganic reductants as ferrous, manganous, nitrite, sulfide and sulfite ions. Ammonia and cyanide also consume considerable residual chlorine, while chlorine substitutes on phenols and other similar aromatic compounds to form chloro derivatives. These materials have varying reaction rates with residual chlorine and these reaction rates are temperature and pH dependent. Rather than consider the free residual chlorine consumed by each of the chlorine demanding substances, we shall assume that all these substances can be lumped together under a single term--chlorine demand. The rate of free residual chlorine consumption can be explained as:

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$$r_c = \left(\frac{dC_F}{dt}\right) = \left(\frac{dC_D}{dt}\right) = -k\left(C_D\right)^m \left(C_F\right)^n \left(pH\right)^p \qquad (5)$$

where:

r_c = rate of free residual chlorine consumption due to chlorine demand

C_D = concentration of chlorine demand

k = rate constant (temperature dependent)

m, n, p = empirical constants

The above rate expression indicates that the rate at which free residual chlorine is consumed by reaction with chlorine demanding substances is proportional to the free residual chlorine concentration, chlorine demand concentration and pH. A simplification of equation (5) would result if a stream is well buffered and the pH remains constant. The rate expression in equation (5) can then be rewritten as:

$$r_c = \left(\frac{dC_F}{dt}\right) = \left(\frac{dC_D}{dt}\right) = -K_D\left(C_D\right)^m \left(C_F\right)^n \qquad (6)$$

where:

$K_D = k\,(pH)^p$ a new rate constant.

In addition to the above chlorine utilization, there may be a depletion of free residual chlorine through chlorine gas escaping to the atmosphere at the air-water interface. This rate of escape can be expressed as

$$r_E = \left(\frac{dC_F}{dt}\right) = -K_G\left(C_C - C_{CA}\right) \qquad (7)$$

where

r_E = rate of free residual chlorine depletion as a result of chlorine gas escape

C_C = chlorine concentration in water

C_{CA} = chlorine concentration in air

K_G = gas escape rate constant

The rate expression in equation (7) states that free residual chlorine depletion due to chlorine gas escape is directly proportional to the chlorine concentration difference at the air-water interface. However, for all practical purposes C_{CA} may be taken as being negligible so that equation (7) reduces to

$$r_E = \left(\frac{dC_F}{dt} \right) = -K_G \, C_C \qquad (8)$$

If we assume the chlorine concentration in water as being in equilibrium with HOCl then by using equation (2) we obtain

$$C_C = \frac{(HOCl) \quad (Cl^-) \quad (H^+)}{K_h}$$

which can be further expressed in terms of free residual chlorine by using equation (4) as

$$C_C = C_F \, \frac{(H^+)}{(H^+) + (K_i)} \quad \left[\frac{(Cl^-) \; (H^+)}{K_h} \right]$$

i.e.

$$C_C = \frac{(H^+)^2 \quad (Cl^-)}{\left[(H^+) \; + \; K_i \right] K_h} \, . \; C_F$$

using this result in equation (8) yields

$$r_E = \left(\frac{dC_F}{dt}\right) = -K_G \left[\frac{(H^+)^2\,(Cl^-)}{\left[(H^+) + K_i\right] K_h}\right] C_F \qquad (9)$$

We have therefore expressed the gas escape depletion rate in equation (9) in terms of the free residual chlorine concentration C_F.

The expressions developed above may now be brought together to give an overall mathematical model describing the temporal and spatial (one-dimensional) distribution of free residual chlorine in a flowing stream. Equation (1) may now be expressed as

$$\frac{\partial C_F}{\partial t} = E\,\frac{\partial^2 C_F}{\partial x^2} - U\,\frac{\partial C_F}{\partial x} + r_C + r_E \qquad (10)$$

which expressed in words is

$$\begin{aligned}\begin{bmatrix}\text{The rate of change}\\ \text{of free residual}\\ \text{chlorine concentration}\\ \text{at a given point in}\\ \text{the stream}\end{bmatrix} &= \begin{bmatrix}\text{The rate of change}\\ \text{of free residual}\\ \text{chlorine concentration}\\ \text{due to turbulent}\\ \text{diffusion at that}\\ \text{point}\end{bmatrix} + \begin{bmatrix}\text{The rate of}\\ \text{change of free}\\ \text{residual chlorine}\\ \text{concentration}\\ \text{due to convective}\\ \text{motion of the}\\ \text{fluid at that}\\ \text{point}\end{bmatrix}\\ &+ \begin{bmatrix}\text{The rate of change}\\ \text{of free residual}\\ \text{chlorine concentration}\\ \text{due to depletion by}\\ \text{chlorine demand}\end{bmatrix} + \begin{bmatrix}\text{The rate of}\\ \text{change of free}\\ \text{residual chlorine}\\ \text{concentration due}\\ \text{to depletion by}\\ \text{gas escape}\end{bmatrix}\end{aligned}$$

Note that the rates r_C and r_E developed in equations (6) and (9), respectively, are included in the model as free residual chlorine sinks.

Section 3.

DEVELOPMENT OF PARAMETER VALUES FROM LABORATORY AND FIELD DATA

In any realistic model, accurate information is not always available for a great many parameters. In order to overcome this lack of information, an experimental program has to be tailored to provide data through which reliable parameter values can be extracted. The model expressed in equation (10) contains seven pertinent constants namely, K_h, K_i, E, K_D, K_G, m and n. Of these constants, K_h and K_i are available in the literature; the remaining constants then must be determined experimentally.

Several simplifications can be made to the model in equation (10) in order to facilitate the computational effort. For instance, when considering streams, the turbulent diffusion, i.e., longitudinal mixing, is generally assumed to be insignificant. This eliminates the first term on the right hand side of equation (10) and the parameter E with it. Another assumption usually made is the steady-state condition which implies no change in free residual chlorine loading with time at a point source. This assumption eliminates the time derivative on the left hand side of equation (10). With these two assumptions, equation (10) is reduced to

$$U \frac{dC_F}{dx} = r_C + r_E \qquad (11)$$

with K_D, K_G, m and n unknown constants. Equation (11) is a simplified version of the original model in equation (10), and it is the starting point for the purposes of estimating model parameters.

Sometimes it is necessary to design small controlled experiments to develop values of specific parameters. These experiments must be controlled to the extent that effects of only a single parameter are studied and all other parameter effects are minimized. For example, in order to evaluate K_D, m and n, the experiment must be designed to minimize the effects of K_G. This means that the experiment should highlight the chlorine demand aspects (K_D dependent) and should minimize the gas escape aspects (K_G dependent).

Determination of K_D, m and n

The rate constant K_D and the constants m and n can be determined by the method of Pseudo Order Reactions, whereby the experimental conditions are varied such that the chlorine concentration is much larger than the chlorine demand or vice versa. In the case of Fields Brook, a situation exists where the chlorine concentration is much larger than the chlorine demand. Equation (6) then reduces to the form

$$r_C = \frac{dC_D}{dt} = -K_D' \left(C_D\right)^m \; ^{**} \qquad (12)$$

To determine K_C' and m experimentally, a batch of the stream water can be dosed with known concentrations of chlorine. The depletion of free residual chlorine then should be measured as a function of time.

Taking logarithms on both sides of equation (11) yields

$$-\ln\left(\frac{dC_D}{dt}\right) = \ln K' + n \ln C_D$$

This expression indicates that a plot of $-\ln\left(\frac{dC_D}{dt}\right)$ V/S $\ln C_D$ will yield a straight line whose slope is n and intercept is $\ln K_D'$; thus both parameters K_D' and n can be evaluated. The $\frac{dC_D}{dt}$ term is obtained by plotting $C_D \cdot {}^{V}/_{S} \cdot t$ and computing the slope of the resulting curve at various values of C_D. Care must be taken in carrying out the above experiment to make sure that the gas escape from the surface of the

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** where $K_D' = K_D (C_F)^n$

water is prevented so that the effect of K_G is eliminated to the maximum extent possible and the depletion in free residual chlorine is solely due to the chlorine demand of the water.

Estimation of K_G

The parameter K_G may be estimated by repeating the previous experiment and this time permitting the surface escape of chlorine gas. The water used in this experiment should be free of chlorine demand so that the depletion in free residual chlorine is solely due to surface escape of chlorine gas. Now from equation (9)

$$-\frac{dC_F}{dt} = K_G\left[\frac{(H^+)^2\ (Cl^-)}{\left[(H^+) + K_i\right] K_h}\right] C_F$$

Therefore a plot of $-\frac{dC_F}{dt}$ V/S C_F should yield a straight line through the origin with the slope being equal to

$$K_G\left[\frac{(H^+)^2\ (Cl^-)}{\left[(H^+) + K_i\right]\ K_h}\right]$$

If values of (H^+), (Cl^-) are measured and K_i and K_h are obtained from the literature, K_G can be determined from the slope.

The K_G measured in the lab can then be related to a K_G' which would be expected in the stream by the following equation (O'Connor, 1958).

$$K_G' = 3.78\ \frac{K_D}{(A/V)} \cdot \frac{S^{1/4}}{H^{5/4}}$$

$$K'_G = \frac{K_D}{(A/V)} \quad \frac{U^{1/2}}{H^{3/2}}$$

for deep streams

where:

A/V = interfacial area between the gas and liquid per unit volume of liquid in the lab

S = slope of the stream

H = average stream depth

U = stream velocity

The above experiments are sketched out primarily to indicate the manner in which parameters can be evaluated through controlled experiments. Several variations and degrees of sophistication are possible both in the experimental stage and the mathematical manipulation. The extent to which this sophistication is carried out would be dictated by the available time, money and manpower resources.

The final test of the model of course is through actual field tests where the laboratory evaluated values of K_D and K_G and n are fine-tuned so that observed data (free chlorine residual, chlorine demand, chloride concentration, pH, temperature and stream depth and velocity or slope) and computed results are very close. Repeated curve fitting runs should be made by varying the parameter values in question to reduce systematic bias. Simply put, the free residual chlorine concentration computed from equation (10) should be compared with observed field measurements of free residual chlorine. If the agreement is poor, the parameter values should be systematically readjusted to close the difference between the observed and the computed results.

In the above context, one can recognize the process of model building as an iterative one in which a proposed model and experimentation lead to data analysis, which in turn leads to further experimentation. This combined approach continues in a presumably converging cycle between analysis and experimentation toward a choice of the most adequate model. Since the investigation cannot be exhaustive in examining all possibilities, no proof exists that the correct model has been found. The investigator must be satisfied that he has determined only the most adequate representation of the experimental data.

SUMMARY

The widespread use of chlorine for disinfection and in industry raises questions as to its toxicity in the nation's waters. At present, little or no predictive capabilities have been developed or utilized to mitigate toxic effects upon aquatic biota. In an attempt to provide a means by which free chlorine residuals may be predicted, the mathematical model expressed in equation (10) was derived. In this expression, the concentration of free residual chlorine at any point in a moving stream has been related to turbulent diffusion, convective motion in the stream at that point, chlorine demand, and gas escape to the atmosphere.

A method by which the necessary parameters can be obtained from laboratory and field experimentation has been suggested whereby the assumptions of a one dimensional, steady state source are employed. Small controlled experiments can then be run in which the gas exchange rate and chlorine demand can be measured under different conditions.

Finally, it is proposed that actual field data can be used to adjust the model empirically. In this way, the predictive capacity of the proposed free residual chlorine model can be tested and verified.

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Dr. J. M. Armstrong, U. of Michigan
Dr. J. Ayers, U. of Michigan
J. Bay, Legislative Serv.Comm.,State House
Dr. A. M. Beeton, Centr.Great Lakes Studies,U.of Wis.
E. Bento, City Mgr.,Ashtabula, Ohio
A. Buchler, City Sanitarian,Ashtabula, Ohio
J. Davis, NY State Geological Survey
Dr. W. Diment, U. of Rochester,Rochester,NY
J. H. Glass, League of Ohio Sportsmen,Columbus,OH
Izaak Walton League of America,Inc.,Ohio Division
League of Ohio Sportsmen, Columbus, Ohio
J. Lesniewicz, Lake Erie Waterfowlers,Toledo,OH
W. Lick, Case Western Reserve U.,Cleveland,OH
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Dr. T. Murphy,DePaul U., Chicago, IL
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Dr. R. Ouellette, Mitre Corp.,McLean, Virginia
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Dr.J. Storr & Dr.K. Stewart,State U. of NY at Buffalo
Dr. R. Sutton, U. of Rochester, Rochester, NY
Dr. P. Michael Terlecky,Calspan Corp.,Buffalo,NY (20)
M. VanLier,Erie County Environ.Mgmt.Council,Buffalo,NY

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